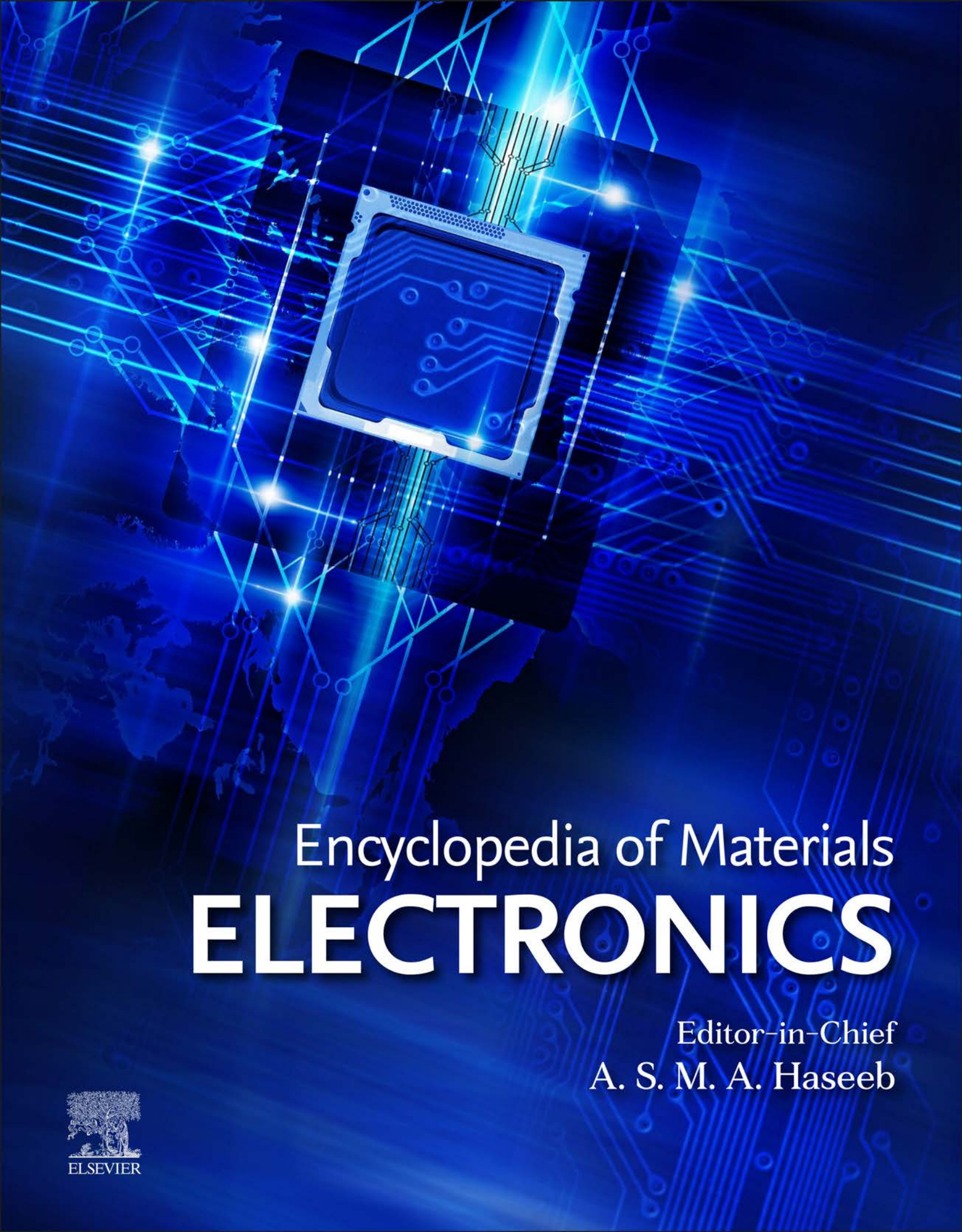




Encyclopedia of Materials **ELECTRONICS**

Editor-in-Chief
A. S. M. A. Haseeb

ENCYCLOPEDIA OF MATERIALS: ELECTRONICS

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Editor-in-Chief

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Volume 3

Sensors, Energy, and Nanoscale Materials

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Dr Chen Jiang is currently an assistant professor, with the Department of Electronic Engineering, Tsinghua University. He received the BS degree in engineering from the Department of Electronic Engineering, Shanghai Jiao Tong University, China, and the Ph.D. degree in Engineering from University of Cambridge, UK. From 2018 to 2021, he was supported by the Wellcome Trust as a Junior Interdisciplinary Fellow at the Department of Clinical Neurosciences, University of Cambridge, UK. His research focuses on novel electronic device architectures, large-area flexible transparent electronics, low-power circuits, and their applications to bioelectronics. Dr Jiang was a recipient of the IEEE Electron Devices Society PhD Student Fellowship 2018.

Manh-Huong Phan



Dr. Manh-Huong Phan is a Full Professor of Physics at the University of South Florida. He received a Ph.D. degree in Engineering Physics from Bristol University, UK in 2006. He is a leading expert in the development of advanced magnetocaloric and magnetoimpedance materials for energy-efficient magnetic refrigeration and smart sensor technologies, respectively. Recently, his group has discovered light-tunable room temperature ferromagnetism in atomically thin van der Waals materials that have the potential to transform the fields of spintronics, valleytronics, opto-spin-caloritronics, and quantum computation. He has published more than 300 peer-reviewed ISI journal papers (over 14,000 citations, *h*-index: 57 from Google Scholar), 10 review papers, 8 book chapters, and 1 textbook. Presently, he serves as Managing Editor/Founding Member for the Journal of Science: Advanced Materials and Devices (IF = 7.38), the Editor for Applied Sciences (IF = 2.838), and the Editorial Board Member of Scientific Reports (IF = 4.379). He received an Honorary Doctorate Degree from Vietnam National University - Hanoi (2021), The USF Outstanding Faculty Research Achievement Awards (2017, 2019, 2021), The USF Outstanding Graduate Faculty Mentor Award (2018, HM), and The Honorary Medal by Vietnam National University - Hanoi (2018). He was also awarded a Certificate of Merit for the Development of Physical Sciences in Vietnam by the Minister of Science and Technology of Vietnam (2021). He has been featured in the list of the World's Top 2 Percent Scientists (2019, 2020, 2021). He has delivered plenary, keynote and invited talks at professional meetings on Magnetism and Magnetic Materials and organized numerous international conferences on Nanomaterials, Energy, and Nanotechnology.

Purushottam Chakraborty



Prof Purushottam Chakraborty received his PhD in Physics from the University of Calcutta and was a Senior Professor at the Surface Physics and Materials Science Division of Saha Institute of Nuclear Physics, Kolkata, India. He was an Honorary Professor of Physics at the University of Pretoria, South Africa. Soon after he had received his PhD degree, he joined the FOM-Institute for Atomic and Molecular Physics, Amsterdam and worked there for two years on "Layered Synthetic Microstructures for the realization of X-UV optical devices", in collaboration with the Philips Research Laboratories, The Netherlands. This is considered pioneering research in the field of "Optics for Soft X-rays to Extreme Ultraviolet". He indigenously constructed a Radio Frequency (RF) Quadrupole Mass Spectrometer (QMS) -based Secondary Ion Mass Spectrometry (SIMS) instrument at Saha Institute of Nuclear Physics and carried out experimental research on Ion-Matter Interactions, Inelastic Ion-Surface Collisions and Ion-Beam Analysis of Materials. His works on "Alkali-metal based Molecular-ion SIMS" have significant relevance to the exact quantification of materials in quantum-confined nanoscale systems. His other research fields include Optical Modifications of Materials, Molecular Beam Epitaxy, Low-dimensional Structures and Nanomaterials, X-UV optics, Optoelectronics, Nonlinear Optics and Photonics.

He has worked as a Visiting Professor at a number of universities and research Institutes, such as, FOM-Institute for Atomic and Molecular Physics (AMOLF), Amsterdam- Netherlands, Universite' Laval - Canada, Osaka Electro-Communication University - Japan, International Centre for Theoretical Physics (ICTP) – Italy, University of Padova - Italy, Friedrich Schiller University - Germany, Catholic University of Rio de Janeiro - Brazil, Sultan Qaboos University, Muscat – Oman, International School of Photonics, India, etc. He delivered invited lectures and plenary talks at more than 160 international conferences across the globe and authored more than 140 scientific papers including invited reviews, monographs and book-chapters. He has edited a book on *'Ion-beam analysis of surfaces and interfaces of condensed matter systems'* (Nova Science, New York) and *Journal of Physics – Conference Series* (Inst. of Physics, UK). Prof Chakraborty has been awarded the **"Most Eminent Mass Spectroscopist of India"** by the Indian Society of Mass Spectrometry and conferred **'Gold Medal'** by the Chairman, Atomic Energy Commission, Government of India. He has received the prestigious **'Premchand Roychand Scholarship'** and **'Mouat Medal'** of Calcutta University. He is an elected Fellow of the Indian Chemical Society and West Bengal Academy of Science and Technology.

Ravinder Dahiya



Ravinder Dahiya is Professor in the Department Electrical and Computer Engineering at Northeastern University, Boston, USA. His group (Bendable Electronics and Sustainable Technologies (BEST)) conducts research in flexible printed electronics, electronic skin, and their applications in robotics, prosthetics, wearables, and interactive systems. He has authored or co-authored more than 500 publications, books and submitted/granted patents and disclosures. He has led or contributed to many international projects.

Prof. Dahiya is currently the President of IEEE Sensors Council. He has been recipient of EPSRC Fellowship, Marie Curie Fellowship and Japanese Monbusho Fellowship. He was the Founding Editor-in-Chief of IEEE Journal on Flexible Electronics and has been editorial boards of several other leading journals. He also founded the IEEE International Conference on Flexible, Printed Sensors and Systems (FLEPS) and has served as General Chair or Technical Programme Chair of

several international conferences. He has received several awards, including Technical Achievement award from IEEE Sensors Council, Young Investigator Award from Elsevier, and 12 best journal/conference paper awards as author/co-author. He is Fellow of IEEE and the Royal Society of Edinburgh.

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Dr. Yang Yang



Yang is an internationally recognized materials scientist with primary interests in surface and interface electrochemistry of energy materials and devices, nanomanufacturing, electrochemical engineering, and nanoscience technology. He focuses on resolving the most challenging issues in energy and sustainability applications of emerging materials, for instance, aqueous batteries beyond Li-ion, direct alcohol fuel cells, water electrolysis, greenhouse gas emission reduction, and waste treatment and recycling.

A general solution to the energy and environmental crisis is to develop sustainable energy systems that can produce and store energy inexpensively and efficiently. To this end, Dr. Yang's lab is dedicated to studying the nano electrochemistry at materials interfaces, interfacial electron transportation in electrochemical systems, and light-materials interaction for solar energy harvesting.

Dr. Yang currently holds the position of Associate Professor at the NanoScience Technology Center, Department of Materials Science and Engineering, Department of Chemistry, Renewable Energy and Chemical Transformation Cluster, and the Stephen W. Hawking Center for Microgravity Research and Education, University of Central Florida.

M. S. J. Hashmi

Professor Hashmi is currently an Emeritus Professor with the School of Mechanical and Manufacturing Engineering at Dublin City University. He established this school and was its Chairman for 25 years until 2012. His research experience, interest and activities are primarily in Materials processing technologies. He earned his MSc, PhD and DSc degrees from University of Manchester and spent 19 years in research and teaching in the UK before taking up the Chair at Dublin City University where he set up the Material Processing Research Centre (MPRC) of excellence in the field of material processing. In 1990 Professor Hashmi established the International Conference Series on Advances in Materials and Processing Technologies (AMPT), a much needed international conference in materials processing. He continues to be the Chairperson of the Steering Committee for this series of conferences. In 1998 he was appointed as Editor-in-Chief of Elsevier Journal of Material Processing Technology and continued in this role until 2008.

Professor Hashmi has supervised and co-supervised 110 PhD and 55 MEng research students to successful completion. He has published in excess of 450 papers and edited 25 scientific books and

is still publishing.

In 2011, he has been appointed by Elsevier as the Editor-in-Chief of its 13 volume, 7,500 pages long Major Reference Works (in Materials Processing Technologies) published in 2014. In the same year Professor Hashmi was appointed again as the Editor-in-Chief for compiling a 3 Volume Major Reference Works by Elsevier on Manufacturing Finishing Processes.

In January 2015 he has been appointed by Elsevier as the Editor-in-Chief for a major on-line publication in Science Direct titled, Reference Module in Materials Science and Materials Engineering, which had 14 main Subject Areas and will contain about 5,000 peer reviewed articles/chapters to be compiled over 4 years. In 2019 he was appointed as the Editor-in-Chief for the 2nd Edition of the Materials Processing Technologies, MRW-MAP2E until 2024.

Currently, Prof. Hashmi is also the Editor-in-Chief for the JAMPT, published by Taylor & Francis Publishers.

Over the years, Professor Hashmi acted as External Examiner & Expert Assessor for PhD candidates and Engineering Departments with universities in Ireland, the UK, India, Pakistan, Bangladesh, Hong Kong, Canada, Australia and Malaysia.

PREFACE

Electronic materials can be considered as the physical basis of the current age of electronics, information and communication technology. These materials, integrated into numerous devices, are widely used in almost all sectors including information and communication technology, automation and control, robotics, manufacturing, process industries, instrumentation, energy and power systems, transportation, healthcare, and defence and security. Electronic materials owe their applications to certain specific properties. These properties are attributable to the flow, control, manipulation and exploitation of electrons; and their interactions with atoms, molecules and electromagnetic radiation. Electronic materials include all major classes of materials: semiconductors, dielectrics, metals, polymers, ceramics, and composites. As a field of scientific research and innovation, electronic materials have been a very active area in the past decades and is expected to grow in importance even further in the coming years.

This encyclopaedia provides advanced level students, researchers, and industry practitioners a wide and deep coverage of the foundational as well as frontier knowledge in the rapidly expanding area of electronic materials which underpin the most influential technologies of our time. The encyclopedia consists of eight sections that deal with Nanoscale Materials for Electronics; Complex Oxides; Magnetic, Spintronic, and Superconducting Materials; Photonic Materials; Organic Electronics; Sensors and Actuators; Materials for Battery and Super Capacitors; and Electroceramics- Piezoelectric, Ferroelectric and Thermoelectric Materials. There are 132 chapters in this encyclopedia. Main highlights of each section are as follows:

- The section on nanoscale electronic materials includes chapters on important materials like zinc oxide, graphene, titanium dioxide. Sol-gel synthesis of nanoscale powder production is covered as well.
- Oxides have established themselves as a very important groups of electronic materials with wide ranging applications in modern technology. The section on oxides covers topics of current interest such as strong electronic correlation in oxides, oxide surfaces and interfaces, high entropy oxides, high temperature superconductors, memristive oxides etc.
- Important topics in modern magnetisms which attract interest from both theoretical and applications points of view are included in the section on magnetic materials. This section comprises spintronics, caloritronics, multiferroics, and tunnelling magnetoresistance.
- Photonic materials are allowing innovation across diverse fields of applications. The section on photonic materials includes a rich variety of chapters. These include nonlinear optical materials, nanophotonics, nanoplasmonics, and biophotonics. Important applied topics in this section also cover photonic integrated circuits, luminescent materials, photonic sensors, and photon sources for quantum technologies.
- Electronic devices based on organic materials are getting increasingly important. The section on organic electronics contains fundamental topics, such as charge transport and mobility in organic semiconductors, single-crystal organic semiconductors, doping in organic semiconductors etc. Promising applied topics include flexible electronics, organic transistors, biocompatible devices etc.
- Sensors are going to be ubiquitous. The section on sensor and actuators comprises topics such as metal-organic framework based chemical sensors, graphene-based touch sensors, disposable pressure sensors, piezoelectric actuators, wearable strain/pressure sensors, biosensor for neurological disorders etc.
- Energy materials are the key to transitioning to our net-zero future. The section dealing with energy materials consists of chapters like MXene pseudocapacitors, advanced characterization of energy materials, metal-organic frameworks for advanced battery, solid electrolytes for lithium-metal batteries etc.
- Electroceramics continue to lead to new technologies serving wide ranging applications. The sections on electroceramics covers topics that include the following: ferroelectric devices, high-power piezoelectric materials, perovskite solar cells, thermoelectric materials, and electrocaloric ceramics.

This major reference work is available online as well as in hardcopies. Each section consists of articles written and edited by leading experts around the world. I am deeply indebted to all the Section Editors for their great efforts in selecting and editing the articles and in maintaining their quality. I highly appreciate the Elsevier team for their professional support at every stage of this work. Finally, I take this opportunity to express my sincere thanks to all authors for their contributions.

It is my hope that researchers, academics, industry professionals and students will find this encyclopedia useful.

Sincerely,
A. S. M. A. Haseeb

Transistor-based Flexible Touch Sensors

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Abstract

This article introduces transistor-based tactile sensing devices. In particular, the piezoelectric oxide semiconductor field effect transistor (POSFET)-based tactile sensing devices are introduced. The state-of-the-art integration of piezoelectric materials on silicon (Si)-based MOSFETs provides the opportunities of detecting dynamic forces. Further, by using chip thinning technologies, it is possible to achieve the devices in flexible form factors. In this regard, this article explains various routes explored for the development of flexible tactile sensing chips.

Key Points

- Transistor-based tactile sensors are presented, particularly Piezoelectric oxide semiconductor field effect transistors (POSFET).
- Piezoelectric materials in relation to tactile sensing are discussed.
- POSFET configurations are introduced: (1) direct deposition of piezo materials; (2) extended gate.
- Thinning technologies that can lead to ultra-thin Silicon-based POSFETs are reviewed.
- Reported POSFETs are summarized, followed by possible future directions.

Introduction

Touch sensing is one of the five fundamental sensory modalities available in the human body. It is critical for the formation of perceptual experience to safely interact with various real-world objects and to build the self-awareness. Considerable efforts have been made to bestow robots with human-like touch sensing capability (Paul *et al.*, 2022; Neto *et al.*, 2022; Kumaresan *et al.*, 2022; Ozioko and Dahiya, 2021). Specifically, tactile sensing has been used in robotics for touch-based environment exploration, human-robot interaction and collaboration, tool manipulation and locomotion, object physical properties' recognition, etc (Murali *et al.*, 2022; Liu *et al.*, 2022; Ntagios and Dahiya, 2022; Murali *et al.*, 2021). The importance of tactile sensing underlines the need for high-quality touch sensors over large-areas and with flexible form factors so that they can conform to curvy surfaces of various parts of robots. In this regard, the first step is to have certain types of tactile sensors with required sensitivity, specificity, uniformity, and reliability similar to the receptors in the human body (Ozioko *et al.*, 2020a,b). So far, various mechanisms have been explored for tactile sensing including piezoelectric, triboelectric, capacitive, piezoresistive and their combination (Dahiya *et al.*, 2010; Ramuz *et al.*, 2012). In addition, the development of sensors needs to be complemented with local processing of data (Dahiya *et al.*, 2019a,b). These attributes could be attained with tactile sensing system on chip, which also holds unrivaled advantage in scalability and reliability (Caviglia *et al.*, 2017).

Historically, transistor-based sensors have been explored since 1970s. The examples include various variants of ion sensitive effect transistors as well as tactile sensing chips (Baghini *et al.*, 2021; Kolesar Jr. *et al.*, 1992; Dahiya and Valle, 2013). Although many already reported tactile sensors are standalone devices, its integration with FETs could provide distinct advantages as better signal-to-noise ratio can be achieved when the tactile transducer is placed close to the amplification block (Dahiya and Valle, 2013). This article discusses the integration of FETs and piezoelectric materials, namely Piezoelectric oxide semiconductor field effect transistors (POSFETs), for tactile sensing. The piezoelectric transducers can mimic the fast-adapting mechanoreceptors present in human skin while the Si MOSFETs could either amplify or locally process the output signal. Owing to the CMOS compatibility, the scalability of POSFET is potentially higher than other strategies explored so far. This presents significant advantages for applications that requires a high spatial resolution, such as electronic skin for robots. However, conventional Si CMOS is rigid and bulky and chip thinning technologies need to be explored to meet the requirement of mechanical flexibility/bendability of POSFET (Gupta *et al.*, 2018). The article starts with the properties of various piezoelectric materials and their suitability for integration with MOSFET device, and then discusses the two configurations of POSFET including the vertically integrated structure and the extended gate structure. The thinning technology that leads to ultra-thin Si-POSFETs is subsequently introduced. This is followed by a discussion in possible future directions of POSFET-like devices.

POSFET (Piezo Materials, Configurations)

Piezoelectric Materials

Various piezoelectric materials that have been studied in relation with tactile sensing can be classified into two categories, i.e., organic and inorganic. The commonly known organic piezoelectric materials are polyvinylidene fluoride (PVDF) and its copolymers, poly(L-lactic acid) (PLLA), glycine, silk, collagen, etc. Among these, PVDF and PLLA are the most investigated. PVDF has been widely studied for energy harvesting and biosensing applications because of its excellent properties such as high piezoelectric coefficient, strong polarity, chemical stability, biocompatibility, and flexibility (Li *et al.*, 2021; Chen *et al.*, 2017). The copolymers of PVDF, such as trifluoroethylene (TrFE), hexafluoropropylene (HPF) and tetrafluoroethylene (TeFE), have been explored (Wei *et al.*, 2018). These polymers require mechanical stretching or additional electrical poling processes to enhance the piezoelectricity by aligning the dipoles with high electric fields (100 V/ μm) (Yogeswaran *et al.*, 2020; Kim *et al.*, 2017; Gupta *et al.*, 2016; Dahiya *et al.*, 2009b). PLLA is a plant-derived flexible and transparent material with great biocompatibility and biodegradability (Hosseini *et al.*, 2021; Nikbakhtnasrabadi *et al.*, 2022). PLLA is also well-known for its large piezoelectric shear constant ($d_{14} = \text{up to } 12 \text{ pC/N}$) (Curry *et al.*, 2020). Hence, PLLA has become a suitable candidate for mobile devices, biosensors and actuators (Zaszczyńska *et al.*, 2020). Owing to its helical structure, PLLA does not require electric poling and instead, the piezoelectricity is induced through thermal stretching to align the randomly oriented molecular chains along the stretched direction (Mishra *et al.*, 2019; Curry *et al.*, 2020). Electrospinning has been explored to be the alternative process to align the bonds (Zhang *et al.*, 2016).

Inorganic piezo materials include aluminum nitride (AlN), lead zirconate titanate (PZT), sodium potassium niobate (KNN), zinc oxide (ZnO), etc. AlN exhibits advantages of being implemented in high frequency applications such as ultrasonic transducers, wide band communications, acousto-optic devices, etc., (Fei *et al.*, 2018; Stach *et al.*, 2015) because of its distinct properties including extremely high thermal stability (melting point: $\sim 2100^\circ\text{C}$, up to 1150°C for piezoelectric effect applications) (Gablech *et al.*, 2020), wide band gap (6.2 eV) (Yu *et al.*, 2021), high acoustic velocity (5760 m/s) (Kaletta *et al.*, 2015), efficient piezoelectric and dielectric properties as well as good compatibility with complementary metal oxide semiconductor (CMOS) technology (Doll *et al.*, 2010). The other popular inorganic piezo material is PZT, which has been most widely used for decades as it possesses a higher sensitivity with a piezoelectric coefficient ($d_{33(\text{PZT})} = \text{up to } 593 \text{ pC/N}$) (Gamboa *et al.*, 2020). However, the presence of toxic lead content in PZT, over 60 wt%, causes potential health and environment hazards, which limits their applications (Zhou *et al.*, 2012). Lead-free alternatives have therefore been studied with materials such as barium titanate (BT), sodium potassium niobate (KNN), etc. However, processing/applications based on BT usually are limited by their Curie temperature (120°C) (Aksel and Jones, 2010). The processing of KNN is challenging, owing to insufficient densification. Additional processes such as doping or pressure-assisted sintering have been introduced to enhance the densification (Ringgaard *et al.*, 2005). Besides, ZnO has also been extensively investigated due to its diversified nanostructures (Dahiya *et al.*, 2022; Shakthivel *et al.*, 2019a; Kumaresan *et al.*, 2022; Shakthivel *et al.*, 2021; Shakthivel *et al.*, 2019b). For example, ZnO nanowires/nanorods have shown outstanding advantages in energy harvesting (Kumar and Kim, 2012), biomedical (Shetti *et al.*, 2019), optoelectronic applications (Djurišić *et al.*, 2010) and printed electronics (Liu *et al.*, 2022). This is because of its excellent properties including wide band gap ($\sim 3.4 \text{ eV}$), high electron mobility, high flexibility, and great biocompatibility and piezoelectric properties (Chorsi *et al.*, 2019). Table 1 shows a comparison of these materials in terms of piezoelectric coefficient, piezoelectric voltage constant, Young's modulus and Curie temperature.

Table 1 Comparison of piezoelectric materials

Material	Piezoelectric coefficient	Piezoelectric voltage constant (g_{33}) ($\text{V} \cdot \text{mN}^{-1}$)	Young's modulus (GPa)	Curie temperature ($^\circ\text{C}$)
PVDF	$d_{33} = -33 \text{ pC/N}$ $d_{31} = 23 \text{ pC/N}$	-0.33	4.18	75–80
PLLA	$d_{14} = 6\text{--}12 \text{ pC/N}$	N/A	2.59	N/A
AlN	$d_{33} = 3\text{--}6 \text{ pC/N}$ $d_{31} = -5 \text{ pC/N}$	0.1	344.83	2100
PZT	$d_{33} = 593 \text{ pC/N}$ $d_{31} = -274 \text{ pC/N}$	0.025	65	350
KNN	$d_{33} = 96 \text{ pC/N}$ $d_{31} = -19 \text{ pC/N}$	0.0469	104	400
ZnO	$d_{33} = 6\text{--}13 \text{ pC/N}$ $d_{31} = -5 \text{ pC/N}$	0.015	201	345 (doped ZnO)
BT	$d_{33} = 190 \text{ pC/N}$ $d_{31} = -78 \text{ pC/N}$	0.0114	67	120
Refs.	(Chorsi <i>et al.</i> , 2019; Habib <i>et al.</i> , 2022; Eawwiboonthanakit <i>et al.</i> , 2014; Gablech <i>et al.</i> , 2020; Vendrell <i>et al.</i> , 2016; Fraga <i>et al.</i> , 2014)			

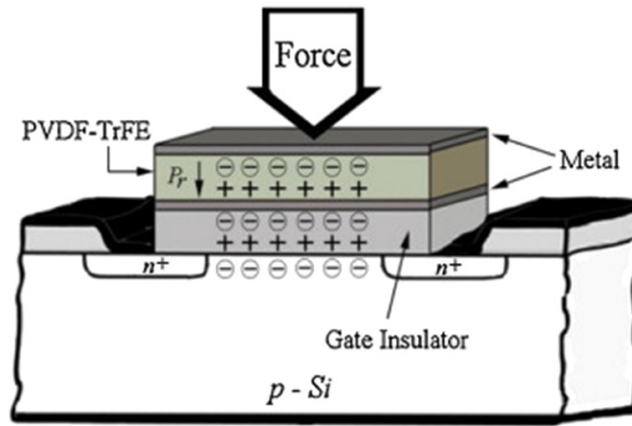


Fig. 1 Schematic of POSFET structure. Reproduced with permission from Dahiya, R., 2009. Touch Sensor for Exploration of Objects and Visuo-Haptic Integration. PhD, University of Genoa. Dahiya, R.S., Valle, M., 2013. Robotic Tactile Sensing – Technologies and System. Dordrecht: Springer Science + Business Media.

POSFET Configurations

Direct deposition of piezoelectric materials

POSFET tactile sensing devices are achieved by integrating the piezoelectric layer on the gate area of metal oxide semiconductor (MOS) devices, as shown in Fig. 1. In this configuration, the remanent polarization (P_r) of the polarized polymer and the charge neutrality lead to an amount of fixed charges ($\pm Q$) in the channel. The charge carriers accumulate at the semiconductor surface. With an external force/stress applied on the device, additional charges are generated on the piezo-sensing layer, which then propagate into the MOSFET channel and modulate the channel current. Therefore, the displacement caused by the contact force is reflected as the current variation in the POSFET channel. The POSFET devices have been developed by directly depositing the PVDF-TrFE as the piezoelectric sensing material on the gate area of the MOS device. These devices show a linear response to dynamic forces under 0.01–5 N with frequencies up to 2 kHz, showing high sensitivity (> 100 mV/N) with a spatial resolution of ~ 1 mm, which is comparable to tactile acuity in the human fingertips (Adami *et al.*, 2012; Dahiya *et al.*, 2009a). As the POSFET device is based on rigid silicon, the silicon piezoresistivity effect also needs to be considered. However, studies have found that it only contributes $\sim 1\%$ of the total output (Dahiya *et al.*, 2009a).

Extended gate

In this configuration, a metal-insulator-metal (MIM) type piezocapacitor is realised separately and connected to the transistors as the extended gate (Fig. 2). Similar to the piezoelectric material directly deposited on the gate area, the extended piezocapacitor, as the extended gate, modulates the charge carriers in the FET channel. In this scenario, even with a short distance between piezocapacitors and MOSFETs (Fig. 2(a)), a considerable substrate capacitance can be introduced, which potentially attenuates the voltage at the gate terminal of the FETs. Alternatively, different piezo-sensing materials have been explored in the off-chip configuration (Fig. 2(b)) such as PVDF-TrFE, AlN, PZT and glycine/chitosan connected to organic FET (OFET) (Hannah *et al.*, 2018), MOFSET (Gupta *et al.*, 2020b; Ma *et al.*, 2022, Gupta *et al.*, 2019) and graphene FET (GFET) (Yogeswaran *et al.*, 2020). The use of transistors based on novel materials provides unique properties to realize POSFET-like systems. For example, by using graphene as the channel material for transistor, a low operating voltage down to 100 mV can be achieved. Nevertheless, towards large-scale fabrication, fundamental challenges associated with the novel materials needs to be addressed as well including material synthesis, transfer, doping, high-quality dielectric formation, etc.

Ultrathin Flexible POSFET

Considering the high-performance requirements, silicon (Si)-based MOSFETs have received major attention. They offer higher mobility, longer shelf life and robustness than the organic counterparts. Nevertheless, conventional MOSFET chips are bulky and rigid, which can hardly be used on the curvature surface, greatly limiting its real-life applications for flexible electronics. This aspect can be resolved by thinning of the chips down to several microns that leads to the flexible, ultrathin system (Christou *et al.*, 2023; Gupta *et al.*, 2018; Navaraj *et al.*, 2018). To give a complete view of the topic, this section describes some of the main thinning methods.

Thinning Technologies

Fig. 3 presents the classification of different thinning technologies for realising UTCs, either based on silicon-on-insulator (SOI) wafers or the bulk Si wafers. In the case of SOI wafers, electronic devices can be dielectrically separated from the Si substrate by

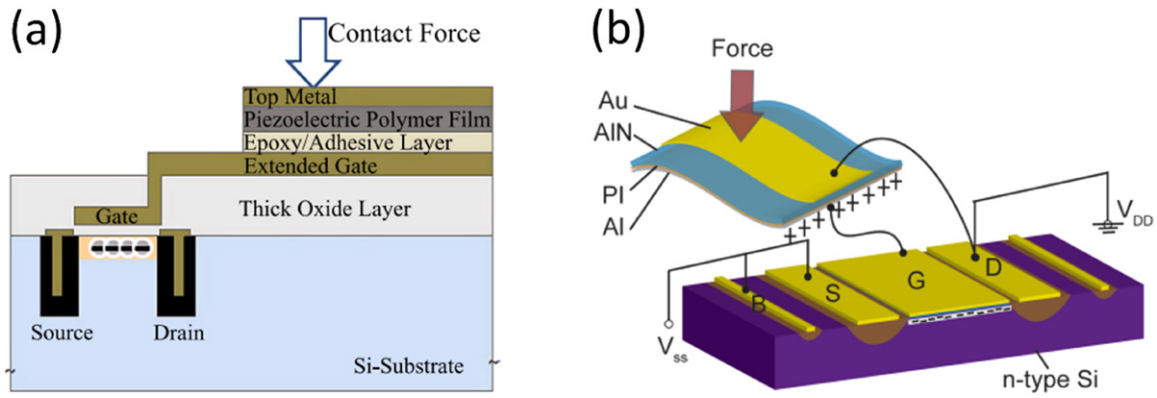


Fig. 2 Schematic of POSFETs in the extended gate configuration: (a) on-chip; (b) off-chip. Reproduced with permission from (a) Dahiya, R.S., Valle, M., 2013. *Robotic Tactile Sensing – Technologies and System*. Dordrecht: Springer Science + Business Media. (b) Gupta, S., Yogeswaran, N., Giacomozzi, F., Lorenzelli, L., Dahiya, R., 2020b. Touch sensor based on flexible AlN piezocapacitor coupled with MOSFET. *IEEE Sens. J.* 20, 6810-6817.

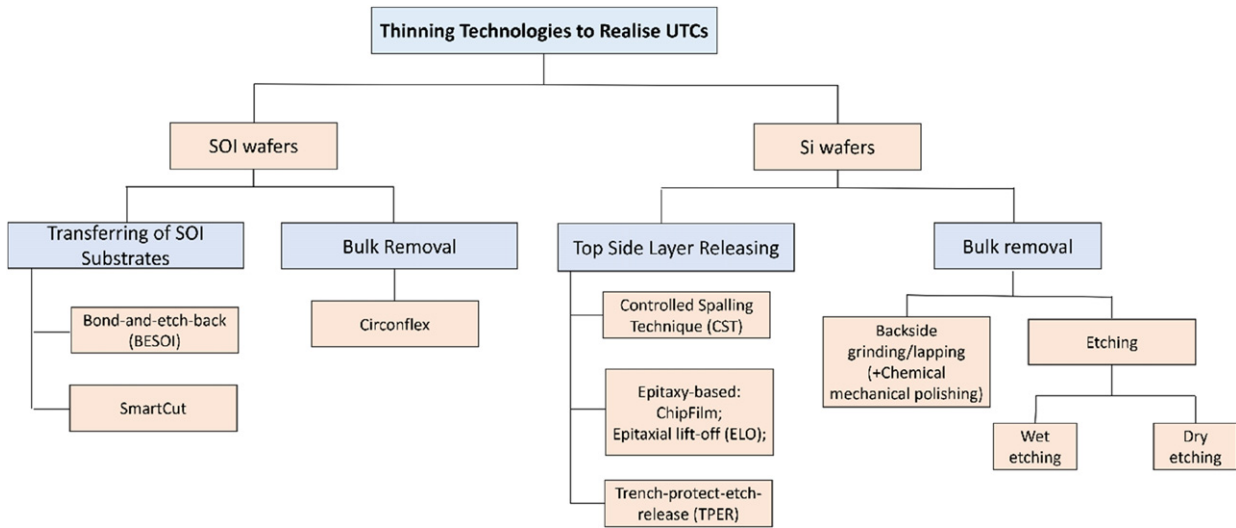


Fig. 3 Classification of thinning technologies to realize UTCs.

creating a buried oxide (BOX) layer. Compared with conventional Si wafers, the SOI wafers offer a higher resistance to latch-up, lower parasitic/junction capacitance and leakage current, etc (Burghartz, 2011). Ultrathin SOI wafers can be obtained by the transfer approach or bulk removal. Most of the SOI manufacturing techniques up to date are based on bond-etch-back SOI (BESOI) (Mizuno *et al.*, 2000) or SmartCut[®] (Schwarzenbach *et al.*, 2016).

Both technologies use BOX as the stopping point to obtain UTCs: (1) trenching the chip down to BOX then selectively removing the BOX; (2) attaching the chip to a temporary wafer with the SOI side facing down, thinning the backside of the Si substrate until BOX, followed by trenching the chip and releasing UTCs from the carrier wafer. BESOI involves bonding two wafers with an insulating layer in between and etching the backside of one of the wafers (Fig. 4(a) and (b)). The use of two wafers per production may be costly, especially with one being wasted. In the case of SmartCut[®] (Fig. 4(c)-(f)), on the other hand, a recyclable handling wafer is used, and the thickness of the other wafer is reduced by splitting (high dose of hydrogen and subsequently high temperature annealing) instead of etching (Celler and Cristoloveanu, 2003). However, the hydrogen implantation induces defects and increases the surface roughness. These two SOI based technologies are also referred as the device-last approach. The obtained ultrathin Si layer has often been used to fabricate devices by a selective removal of BOX layer and selectively etching of the top layer for forming thin single crystal Si structures such as micro-/nanoribbons, then transferring printing them to flexible substrates for further device fabrication (Menard *et al.*, 2004; Yuan *et al.*, 2009).

Circiflex is a device-first approach. The schematic of the process flow is shown in Fig. 5. The polyimide film is used to cover the already fabricated devices on the SOI wafer, except the wafer edge, and a temporary glass carrier is attached to the sample with adhesive. Last, the bulk Si is selectively removed and the ultrathin Si layer is released by trenching the wafer edges (Dekker *et al.*, 2005). The merit of SOI technologies is that nanometer thickness is possible to be achieved. However, multiple complex processes are inevitable, and the high manufacturing cost may hinder the further process of such techniques for industrial scale manufacture. In addition, with such thin

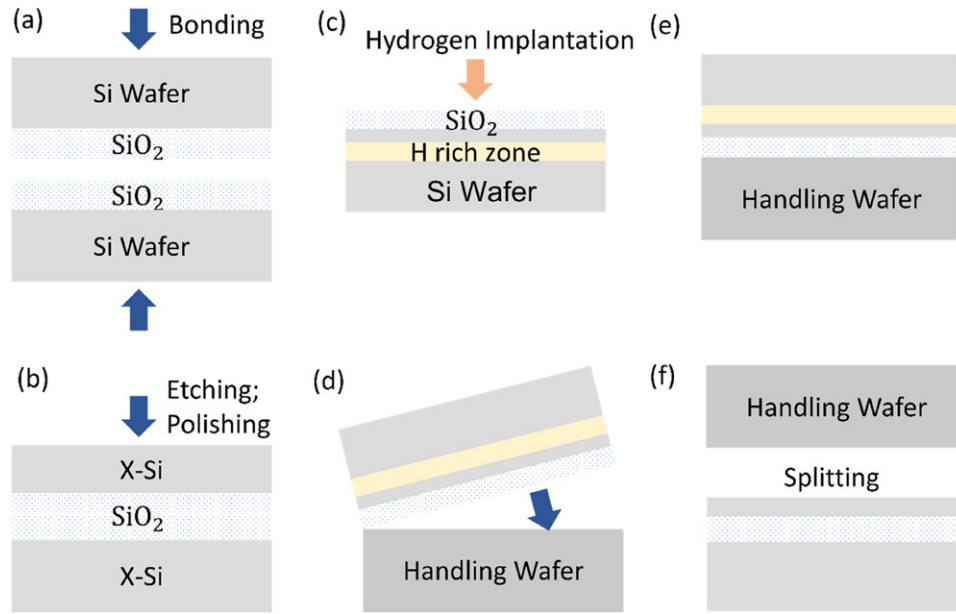


Fig. 4 Schematic of SOI technology based on BOX removal: (a) and (b) BESOI process; (c)-(f) SmartCut® process.

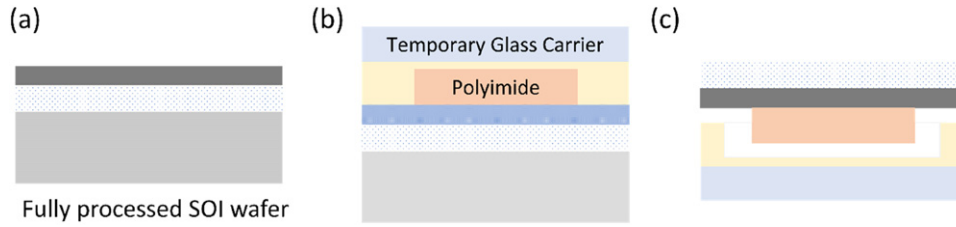


Fig. 5 Schematic process of Circonflex technology.

thickness, the thermal conductivity of nanoscale Si is expected to be half of the undoped bulk Si, which could result in poor heat dissipation and require extra heat management (Ju and Goodson, 1999). Moreover, the dependence of mobility on temperature also needs to be taken into consideration, as higher temperature could lead to lower mobility (Klaassen, 1992).

The bulk Si wafers offer a more cost-effective alternative to process in UTC technology. Bulk Si-based thinning technologies are normally classified into two categories: (1) releasing the top layer; (2) removing the bulk Si from the backside. Controlled spalling technique (CST), also referred as Slim-Cut, has been explored as one of the top layer releasing approaches. In this case, the top thin Si layer is achieved by inducing a fracture to propagate the crack in parallel to the wafer surface (Fig. 6(a)). To prevent the formation of the cracks, a tensile stressor layer is introduced in this technique. Owing to the induced upward shear force, the top thin Si layer can be removed from the bulk substrate. This method, although challenging, could control the thickness of the desired top layer and fracture depth by taking advantage of the stressor layer material. UTCs can also be obtained using the trench-protect-etch-release (TPER) method (Fig. 6(b)). Deep reactive-ion-etching (DRIE) is used to form the deep trenches. A soft mask (photoresist) and hard mask (SiO₂) are used to protect the device side of the wafer, along with aluminum oxide (Al₂O₃) deposited by atomic layer deposition (ALD) to cover all other sides of the sample. Al₂O₃ on the backside of the wafer is etched using RIE and the wafer is subsequently etched using XeF₂, which leads to the formation of spheres merging with neighboring spheres and therefore the release of a top Si layer. In addition, the remaining bulk wafer can be re-used after polishing using chemical mechanical polishing (CMP), which reduces the overall process cost. Epitaxy-based top Si layer releasing is another approach that has been studied, such as Chipfilm technology and epitaxial lift-off (ELO). By introducing a sacrificial layer (e.g., a porous Si or epitaxially grown layer) between the bulk wafer and top Si layer, the removal of the desired top layer can be realised either physically or chemically (Fig. 6(c)). The advantages of this technical is a precise control over the desired thickness of the top Si layer.

The other category of Si-UTC technology is focussed on removing the bulk substrate after the device fabrication on the front side, usually assisted with a protective layer for the top side, including backside lapping/grinding (Kumaresan et al., 2021), wet etching (Navaraj et al., 2018), dry etching (Burghartz et al., 2010), or a combination of all.

Backside lapping/grinding (Fig. 7(a) and (b)) is usually preferred because of a higher throughput than the other techniques and good surface flatness of the desired thin chips (Vilouras et al., 2020). Backside mechanical thinning is usually conducted with 2

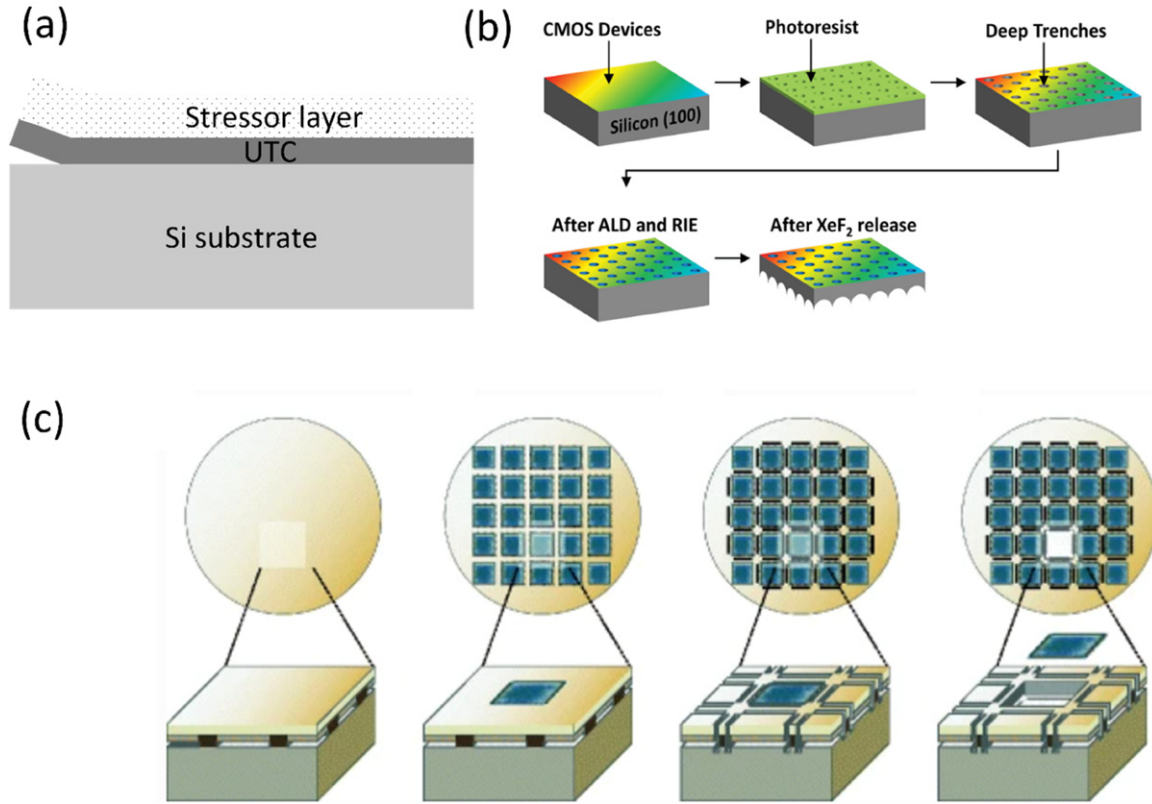


Fig. 6 Schematic of UTC Si-based technology by releasing top layers: (a) Controlled Spalling Technique (CST); (b) Trench-protect-etch-release (TPER). (c) ChipFilm technology. Reprinted with permission from (b) Hussain, A.M., Hussain, M.M., 2016. CMOS-technology-enabled flexible and stretchable electronics for internet of everything applications. *Adv. Mater.* 28, 4219-4249. Copyright John Wiley & Sons. (c) Zimmermann, M., Burghartz, J.N., Appel, W., Harendt, C., 2011. Fabrication of ultra-thin chips using silicon wafers with buried cavities. In: Burghartz, J. (Ed.), *Ultra-Thin Chip Technology and Applications*. New York, NY: Springer. Copyright Springer.

steps: (1) Coarse thinning for a rapid removal rate; (2) Fine thinning for obtaining a smooth surface with a relatively slower etch rate. The main disadvantage is that high mechanical stress is induced in the Si crystal structure, potentially leading to wafer warpage or even breakage. Therefore, different stress-relief methods have been explored, such as using a sacrificial layer (described in Section “Ultrathin Silicon Based POSFET With the Extended Gate”), etching (introduced below), dicing before grinding (DBG), or stealth dicing before grinding (SDBG). In the case of DBG, wafers are partially grooved before grinding. After grinding, the final thickness can be less than those realised by dicing after grinding (DAG) with a less chance of breakage. However, blade sawing and tape removing can both potentially induce wafer chipping. The potential issues created by mechanical interaction during DAG and DBG can be overcome by SDBG where the laser process is implemented internally (Teh *et al.*, 2015). SDBG can be conducted in a high speed by a complete dry process without giving rise to chipping and debris pollution. The disadvantages of SDBG process include that metals and dielectrics may not be separated completely, and tapes need to be expanded during the process, which decreases the effectiveness, and increases the overall cost owing to the use of additional tools (Kumagai *et al.*, 2007).

Chemical mechanical polishing (CMP), also referred as chemical mechanical polarization, has also been used to improve the surface quality after the major removal of the bulk substrate (Fig. 7(c)). As a synergetic thinning method where unwanted materials in atomic scale can be removed by chemical etching for a desirable flatness, CMP can be a part of an integrated thinning process to reduce the non-flatness generated from previous procedures (Li *et al.*, 2016).

In addition to the previously mentioned mechanical based processes, chemical etching can be further employed to reduce the wafer thickness. Compared to the mechanical based process, chemical etching is less likely to be affected by crystalline defects and microcracks because of less residual stress on the wafer. The chemical etching includes wet and dry processes. For wet etching, aqueous solution is employed to dissolve the Si wafer. For this, two kinds of solutions are used that can provide isotropic or anisotropic results. Solutions containing nitric acid (HNO_3) and hydrofluoric acid (HF) can lead to isotropic wet etching, which is orientation independent but could potentially cause under-etching (Köehler, 2013). The reaction of Si oxidation by HNO_3 and dissolution by HF are shown as follows:



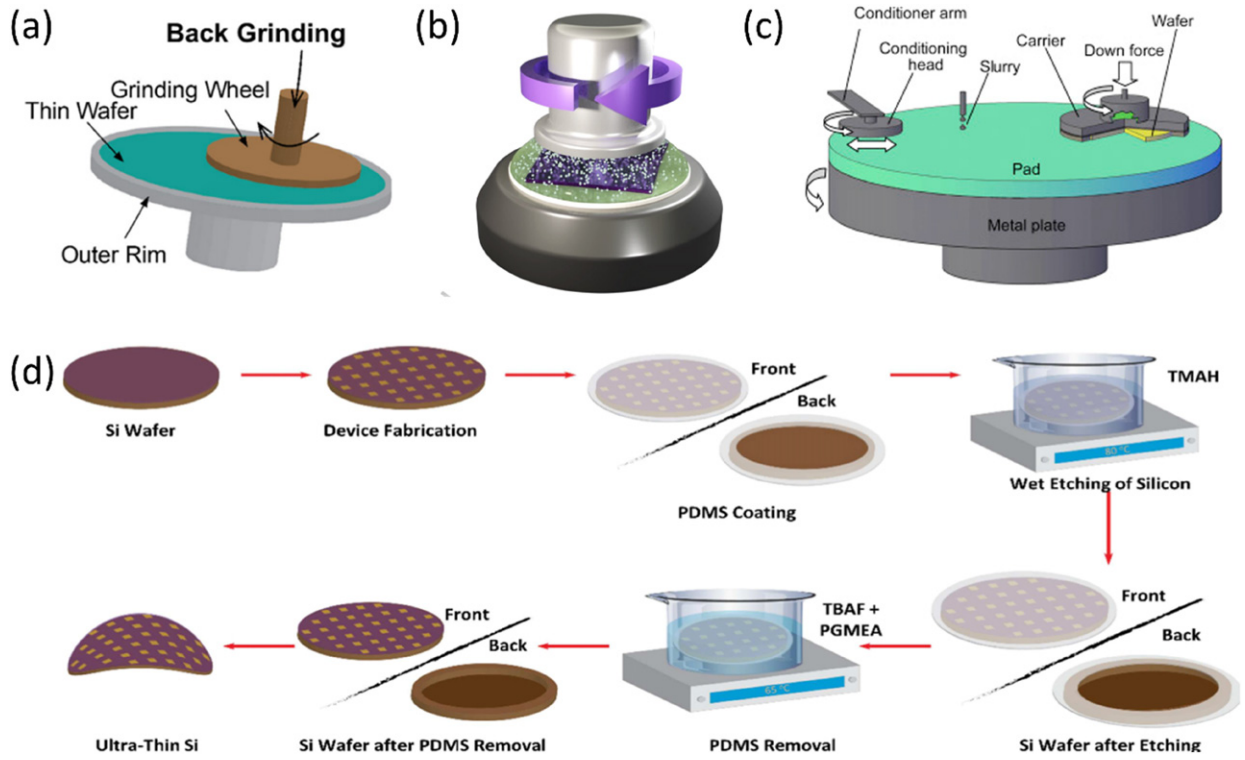
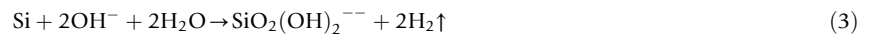


Fig. 7 Schematic of Si-UTC technology for bulk removal: (a) Backside grinding (Gupta *et al.*, 2018); (b) Backside lapping (Christou *et al.*, 2023); (c) Chemical mechanical polishing (d) Wet chemical etching. Reprinted with permission from (a) Gupta, S., Navaraj, W.T., Lorenzelli, L., Dahiya, R., 2018. Ultra-thin chips for high-performance flexible electronics. *npj Flex. Electron.* 2, 8. (b) Christou, A., Ma, S., Zumeit, A., Dahiya, A.S., Dahiya, R., 2023. Printing of nano to chip scale structures for flexible hybrid electronics. *Adv. Electron. Mater.* 2201116 (c) Li, Z.C., Baisie, E.A., Zhang, X.H., Zhang, Q., 2016. Chapter 13 – Diamond disc pad conditioning in chemical mechanical polishing. In: Babu, S. (Ed.), *Advances in Chemical Mechanical Planarization (CMP)*. Woodhead Publishing. Copyright from Science Direct; (d) Gupta, S., Vilouras, A., Dahiya, R., 2020a. Polydimethylsiloxane as polymeric protective coating for fabrication of ultra-thin chips. *Microelectron. Eng.* 221, 111157.

Anisotropic wet etching, usually involves etchants such as potassium hydroxide (KOH), ethylene diamine-pyrocatechol (EDP), tetra methyl ammonium hydroxide (TMAH) (Angelopoulos and Kaiser, 2011). The chemical reaction in anisotropic wet etching is separated into an oxidation reaction and a reduction reaction, and the simplified reaction can be expressed as Eq. (3):



Despite admirable uniformity, KOH is not widely adopted since the high diffusion rate of potassium ions in silicon is incompatible with electric circuits (Toofan and Toofan, 2015). EDP is also rarely employed because of its toxicity, unsteadiness, and challenges associated with handling. A metal-ion free etchant, TMAH, performs better by providing a decent etching uniformity and high selectivity (Ronchin *et al.*, 2004). Anisotropic etching often causes pyramid shaped hillocks of the material surface, which can be prevented by adding IPA in the etchant to decrease the formation of hydrogen bubbles.

Dry etching is a thinning method that is run in a reactive ion atmosphere. Similar to chemical etching, it is well-known for not giving rise to edge chipping as mechanical pressure is not involved. It is also not likely to cause mask undercutting which has been observed in the isotropic wet etching process. To be specific, there are various types of dry etching processes, including reactive ion etching (RIE), reactive ion beam etching (RIBE), ion beam etching (IBE), barrel etching and reactive sputter etching (RSE) (Sengupta *et al.*, 2019). RIE is the most common type of dry etching where it combines the anisotropic or directional ionic bombardment and isotropic chemical reactions. U-grooves are generated after dry etching and replace the sharp crack tip, giving rise to less stress concentration and diminishing the surface roughness. Due to the relatively low etch rate using chemical or dry etching, they are mostly used as a stress-relief thinning approach after the completion of the mechanical grinding. Table 2 summarises a comparison between different thinning technologies regarding their challenges.

Ultrathin Silicon Based POSFET With the Extended Gate

The abovementioned thinning technologies are the key to achieve Si-UTCs. By reducing the bulk Si thickness, originally rigid Si chips become thin and bendable, which provides the opportunities for extending the system functionalities to applications such as electronic skin and other flexible electronic applications.

Table 2 Comparison of different thinning technologies regarding their challenges

Technologies	Challenges	References
SOI Wafer based	(1) Higher cost for SOI processing than Si wafers (2) Complexity and difficulties of fixing, transferring and supporting UTCs during the removal process of the remaining wafer	(Burghartz, 2011)
Controlled Spalling Technique (CST)	(1) Extra tensile stress induced by the deposition of the stressor layer, potentially shifting the Si band structure, therefore changing the effective mass of carriers and carrier mobility (2) Difficulty of controlling the desired top layer thickness (3) Wafer warpage due to the tensile stress even after removing the stressor layer	(Yu <i>et al.</i> , 2008, Gong, 2021)
Epitaxy-based: Chipfilm Technology, Epitaxial lift-off (ELO)	Time consuming, low throughput and costly due to the use of epitaxy	(Hussain and Hussain, 2016)
Trench-Protect-Etch-Release (TPER)	The space available for device fabrication is reduced because of the creation of holes due to the trench formation	(Hussain and Hussain, 2016)
Backside grinding/lapping	High stress induced in the crystal structure; stress-relief methods often needed	(Kumaresan <i>et al.</i> , 2021)
Chemical/wet etching	Time consuming, mask undercutting for isotropic etching or hillock formation on the surface for anisotropic etching	(Navaraj <i>et al.</i> , 2018)
Dry etching	High cost, low throughput, non-uniform surface	(Kazmi <i>et al.</i> , 2013)

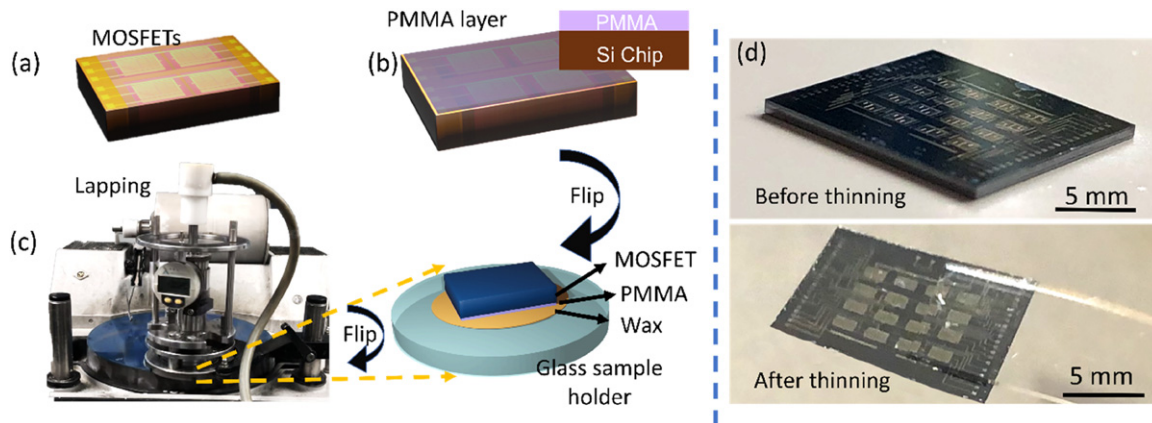


Fig. 8 (a) – (c) Backside lapping thinning process assisted with PMMA sacrificial layer; (d) Photograph of MOSFET chip before and after thinning. Reproduced from Ma, S., Kumaresan, Y., Dahiya, A.S., Dahiya, R., 2021. Ultra-thin chips with printed interconnects on flexible foils. *Adv. Electron. Mater.* 8, (5), 2101029.

Ultrathin Si-based POSFET in the extended gate configuration has been explored in past (Ma *et al.*, 2022). To achieve so, research has first focused on achieving the bendability of Si-based chips. Backside lapping technique has been conducted for this study because of the rapid removal rate and relatively lower cost compared with other techniques as mentioned above. Despite the maturity of the lapping technique, handling ultrathin chips (UTCs) with a thickness under $50\ \mu\text{m}$ is challenging, as it easily leads to chip breakage. Backside lapping, in comparison with grinding, offers a gentler process as loose abrasive slurry is used instead of fixed abrasive wheels. Consequently, a smoother surface can be effectively achieved (Pei *et al.*, 2004). During the lapping process, chips are attached to a sample holder using low stress wax. The challenge of this approach lies in the separation process when UTCs need to be removed from the sample holder after thinning. During the removal process, when samples need to be heated to melt the wax, UTCs under $50\ \mu\text{m}$ thickness are prone to breakage due to its fragile nature. A novel and cost-effective stress-relief method has been reported by employing polymethylmethacrylate (PMMA) as a sacrificial layer between UTCs' front sides and the adhesive wax. By doing so, it protects the front/device side of the chip from impurities during thinning and drastically reduces the internal stress (four orders of magnitude lower) on the chip in the debonding process after thinning (Kumaresan *et al.*, 2021). Besides, PMMA is a more cost-effective option. In industry, back thinning processes are usually assisted by using UV tapes to protect the semiconductor devices and the adhesion of UV tapes are controlled by irradiating UV light for an easy separation. However, they are more costly. For example, to coat a 6-in wafer, it requires the use of $\sim 6\ \text{ml}$ PMMA, corresponding to a cost $\sim \$0.3$. This is less than one third of the cost by using an UV tape ($\sim \$1$) (Patil *et al.*, 2019). Additionally, the delamination of the UV tape may cause wafer damage which further adds additional cost. This highlights the advantage of using PMMA as the protection layer. For a direct understanding, the optimized thinning process is briefly described as follows

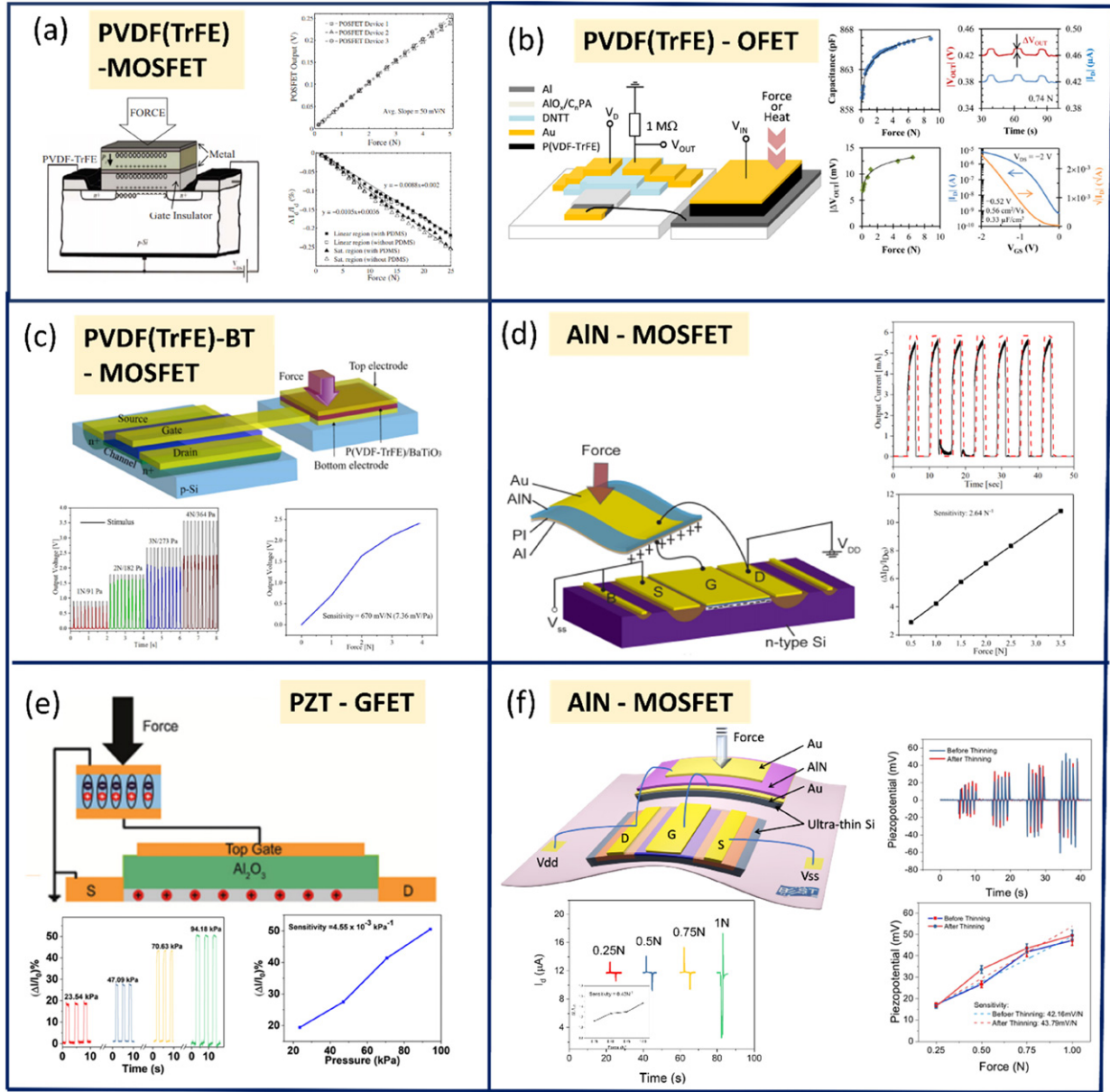


Fig. 9 Reported POSFETs with different configurations including schematics and sensing results: (a) The vertical integration using PVDF(TrFE) with MOS devices; (b)-(f) The extended gate configuration: (b) PVDF(TrFE) with OFET; (c) PVDF(TrFE)-BT with MOSFET; (d) AlN with MOSFET; (e) PZT with GFET; (f) AlN with MOSFET. Reproduced from (a) Dahiya, R.S., Metta, G., Valle, M., Adami, A., Lorenzelli, L., 2009a. Piezoelectric oxide semiconductor field effect transistor touch sensing devices. *Appl. Phys. Lett.* 95, 034105. (b) Hannah, S., Davidson, A., Glesk, I., *et al.*, 2018. Multifunctional sensor based on organic field-effect transistor and ferroelectric poly(vinylidene fluoride trifluoroethylene). *Org. Electron.* 56, 170-177. (c) Gupta, S., Shakhthivel, D., Lorenzelli, L., Dahiya, R., 2019. Temperature compensated tactile sensing using MOSFET with P(VDF-TrFE)/BaTiO₃ capacitor as extended gate. *IEEE Sens. J.* 19, 435-442. (d) Gupta, S., Yogeswaran, N., Giacomozzi, F., Lorenzelli, L., Dahiya, R., 2020b. Touch sensor based on flexible AlN piezocapacitor coupled with MOSFET. *IEEE Sens. J.* 20, 6810-6817. (e) Yogeswaran, N., Navaraj, W.T., Gupta, S., *et al.*, 2018. Piezoelectric graphene field effect transistor pressure sensors for tactile sensing. *Appl. Phys. Lett.* 113, 014102. (f) Ma, S., Kumaresan, Y., Dahiya, A.S., Lorenzelli, L., Dahiya, R., 2022. Flexible tactile sensors using AlN and MOSFETs based ultra-thin chips. *IEEE Sens. J.* 1, (1).

(Fig. 8(a)-(c)): Firstly, a $\sim 20 \mu\text{m}$ thick PMMA layer is spin-coated on the chip's front side. The device is then firmly attached to the glass sample holder using melted low-stress wax with the device side facing down. After the wax becomes solidified again (about 30 m at room temperature), the sample is placed onto the lapping jig through vacuum with the jig positioned on the lapping plate. During thinning, the lapping plate is set at 25 rpm with the slurry (a mixture of water and aluminum oxide (Al_2O_3) powder with $15 \mu\text{m}$ diameter) running on the lapping plate. Subsequently, the UTC is removed from the glass sample holder by heating the sample to melt the wax on the hot plate. Last, PMMA is removed by using acetone. Assisted by the PMMA sacrificial technique, UTCs down to $35 \mu\text{m}$ thick have been successfully achieved, as shown in Fig. 8(d).

Table 3 Comparison of POSFET type touch sensors

Configuration	Piezosensing material	FET structure	FET carrier mobility ($\text{cm}^2/\text{V} \times \text{s}$)	Force sensitivity (N^{-1})	Force sensing range (N)	Flexibility	References
Vertical integration	PVDF-TrFE	MOSFET	N/A	5	<5	Rigid	(Dahiya <i>et al.</i> , 2009a)
Extended Gate	PVDF-TrFE	OFET	0.56	8.12	<6.5	Rigid	(Hannah <i>et al.</i> , 2018)
Extended Gate	P(VDF-TrFE)-BT	MOSFET	705	7.44	<4	Rigid FET Flexible sensor	(Gupta <i>et al.</i> , 2019)
Extended Gate	AlN	MOSFET	695	2.64	<3.5	Rigid FET Flexible sensor	(Gupta <i>et al.</i> , 2020b)
Extended Gate	PZT	GFET	$\mu_h = 879$; $\mu_e = 828$;	71518	<5990	Rigid	(Yogeswaran <i>et al.</i> , 2018)
Extended Gate	AlN	MOSFET	780	0.43	<1	Flexible	(Ma <i>et al.</i> , 2022)

The key parameters such as threshold voltage, subthreshold swing, peak transconductance, peak mobility and current on/off ratio, have been extracted and compared, and the reliability of the optimized thinning technique has been proven by demonstrating no degradation of the device performance compared with the original thickness (520 μm) (Ma *et al.*, 2021). To realize POSFETs in the extended gate configuration, the performance of UTC-based AlN piezocapacitor pressure sensors has also been studied, showing negligible changes in sensitivity ($\sim 3.7\%$) after thinning. After confirming the device performance after thinning for both MOSFET and AlN UTCs, they are then integrated on a single flexible polyimide substrate to form bendable Si-UTC based POSFET tactile sensor in the extended gate configuration (Fig. 9(f)). The connections between the UTCs having transistors and the extended gate piezocapacitor can be realised using direct printing of metal inks (Ma *et al.*, 2021).

Table 3 summarises a comparison of reported POSFETs with different configurations, piezo-sensing materials, FET structures, force sensitivity and flexibility. Most of the reported studies have focused on the extended gate configuration, comprising of the piezoelectric pressure sensor in MIM structure coupled with FETs. However, the extended gate configuration has its merit by ensuring that the mechanical stress is applied to the transducer only and prevents the mechanical stress related variations in the output of FET devices (Fig. 9(b)–(f)). For example, if PVDF (and its copolymers) or PZT as the piezo-sensing material is directly present on the gate area of the transistor, then force applied on the piezoelectric material could also lead to piezoresistance related variation in transistors output. Further, the required poling/stretching process may cause additional stress and hence variations in the output of FETs. Among the ones featured the extended gate configuration, PZT-GFET presented the highest force sensitivity (Fig. 9(e)) (Yogeswaran *et al.*, 2018). This could be because of the chosen piezo sensing material's intrinsic properties such as high piezoelectric coefficient of PZT ($d_{33} = 593\text{pC/N}$). However, as stated before in Section "Piezoelectric Materials", PZT is not always preferred sensing material owing to the presence of high lead content. Devices based on PVDF show a modest sensitivity (Fig. 9(a)–(c)), but poling/stretching is usually needed during processing. AlN, on the other hand, is biocompatible and biodegradable, does not require any poling/stretching. However, its piezoelectric coefficient is relatively lower, which results in a lower sensitivity in the POSFET (Fig. 9(d) and (f)). In addition, despite the good sensitivity of PVDF-OFET (Fig. 9(b)), OFET presents over two orders lower in mobility compared with the other FETs. Higher carrier mobility is also essential for POSFET applications as it ensures high device performance with fast response under dynamic circumstances. Nevertheless, considering the normal manipulative tasks for humans take up to 0.9 N (Dahiya *et al.*, 2009a), all reported devices show the capability of detecting within such range of force.

Future Directions

Although studies have shown good progress in realising POSFETs in the extended gate structure, the vertically integrated POSFET configuration may have distinct advantages including reduced device space, higher density, better suitability for large areas, which is essentially required to achieve robotic applications. In addition, reduced numbers and lengths of interconnects could lead to an enhanced signal-to-noise ratio and are better suited for real-life applications.

Whilst the planar POSFETs with vertical integration (i.e., piezoelectric material directly integrated on the gate area) have shown the potential, their flexible versions are yet to be reported and are worth investigating. Aspects such as high spatial resolution, high density, sensing materials capable of recording dynamic contacts, multifunctionality, wider bandwidth, better force sensitivity, etc., should be taken into consideration to achieve high performance large area POSFETs, as indicated in Fig. 10. Potential challenges may include the integration or deposition of the piezo-sensing material directly on the gate region with high density and resolution. From the Si-UTC point of view, with the vertical integration of piezo-sensing material, when contact pressure is applied to the sensing area, whether UTC piezoresistive behavior contributes to the final output needs to be investigated too. Another future aspect is to create a POSFET array/matrix to potentially have the capability of detecting both normal and tangential component of the contact force.

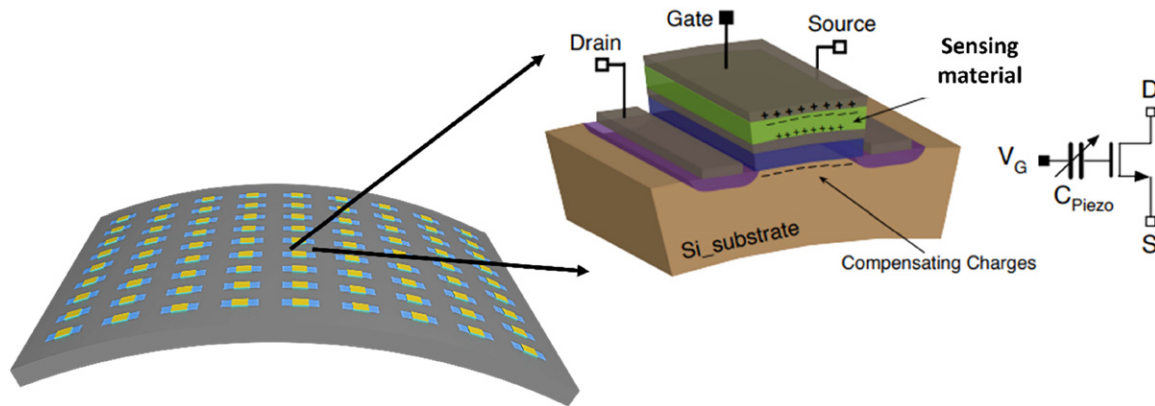


Fig. 10 Schematic of future bendable on-chip POSFET array.

Conclusions

In conclusion, this article discusses the concept of POSFET tactile sensing devices, piezoelectric sensing materials, POSFET configuration, thinning technologies that help achieve bendability and the challenges in realising ultrathin Si-based devices, as well as future aspects of POSFET systems. The merits of such marriage between sensing unit and the transistors have been presented. Up to date, flexible POSFETs have only been studied in the extended gate configuration. As the bendability issue has been addressed with optimized thinning processes, other challenges such as achieving high density by directly depositing sensing materials still require more attention. With future aspects implemented, a POSFET-network with the complete flexibility can potentially become the mechanoreceptors for electronic skin for robotic applications with the capability of sensing and processing tactile data on site.

Acknowledgments

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Magnetic Sensors: Principles and Applications

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Introduction

Magnetic sensors are used to detect magnetic fields in the form of flux, strength and directions. Detection of magnetic field and its measurement have always been an essential function in many applications for years (Lei *et al.*, 2013; Trifon and Chong, 1999). Data obtained from magnetic sensors (changes and alterations of magnetic field) can be utilized to monitor the positions, directions, rotations and angles of objects, presence of electric current etc. For this reason, magnetic sensors find applications in automobiles, military, robotics, medical devices, space equipment, geophysics, industrial measurements and so on. New magnetic sensors with multi-functional capabilities and robustness are widely required and main key technological requirements for many applications.

So far, different types of magnetic sensors such as Hall sensors, semiconducting magnetoresistors, ferromagnetic magnetoresistors, fluxgate sensors, superconducting quantum interference device (SQUID), resonant sensors, induction magnetometer, linear variable differential transformer, inductosyn, synchros and resolvers, Eddy current sensors, variable reluctance sensors, magnetic encoders, permanent magnet linear contactless displacement sensors, magnetoresistive position sensors, reed contact, Wiegand wires, magnetic force and torque sensors, magnetic flowmeters and current sensors have been developed for different applications. Out of that, Hall sensors are one of the most widely used sensors for detecting magnetic fields (Behet *et al.*, 2000). However, in the recent years, anisotropic magnetoresistive (AMR) sensors with integrated flipping and feedback coils have become standard off-the-shelf devices for the use in medium-accuracy applications such as compasses for mobile devices (Rao *et al.*, 2018; Ripka and Janosek, 2010). The AMR sensors have 100 times higher field resolution compared with the Hall sensor with same size and power consumptions (Ripka, 2008).

After many years of research and developments, giant magnetoresistive (GMR) sensors are being used as hard disk data reader, biosensors, microelectromechanical systems (MEMS) and current sensor in smart grid (Ouyang *et al.*, 2019; Reig *et al.*, 2013; Shen *et al.*, 2018). Spin-dependent tunneling (SDT) sensors are being used for applications that require the smallest size for sensor (Ripka and Janosek, 2010). Another important sensing device is the fluxgate sensors (Lei *et al.*, 2018; Lenz, 1990; Primdahl, 1979; Ripka, 2000; Setiadi and Schilling, 2019), which is basically a vector device to measure DC or low-frequency AC magnetic fields (Ripka, 2003). Fluxgate sensors are being used as ferromagnetic matter detectors, magnetic ink reader, current sensors and non-destructive tester (Kaluza *et al.*, 2003). The giant magnetoimpedance (GMI) sensors are based on field-dependent change of the penetration depth (Knobel *et al.*, 2003). The GMI sensors have few practical applications as it gives weak, temperature-dependent signals and the characteristics are non-linear and uni-polar. Despite the recent achievements in GMI and orthogonal fluxgate sensors, these devices show inferior performance compared to the classical longitudinal fluxgate sensors (Ripka and Janosek, 2010).

The development of magnetic sensor technology is slow but gradual (Ripka and Janosek, 2010). In this article, a review on the recent advances in the technology and applications of magnetic sensors has been presented. The common magnetic sensors such as magnetic field sensors, magnetic position and distance sensors, magnetic proximity switches are discussed briefly. Some general applications of magnetic sensors are presented at the end of the article.

Principles for Magnetic Sensing

There are different types of magnetic sensors such as Hall sensors, semiconducting magnetoresistors, ferromagnetic magnetoresistors, fluxgate sensors, superconducting quantum interference device (SQUID), resonant sensors, induction magnetometer, linear variable differential transformer, inductosyn, synchros and resolvers, Eddy current sensors, variable reluctance sensors, magnetic encoders, permanent magnet linear contactless displacement sensors, magnetoresistive position sensors, reed contact, Wiegand wires, magnetic force and torque sensors, magnetic flowmeters and current sensors. Each of the sensors has different approaches and technology to detect magnetic field. The techniques used to create these sensors involve various combinations of physics and electronics. For example, in Hall sensors magnetic field is measured from the output voltage which is proportional to the strength of magnetic field. On the other hand, magnetoresistive devices measure the magnetic field from the electrical resistance. Fluxgate sensors measure magnetic fields by measuring the response of an internally created magnet that runs through a continually fluxing set of parameters.

Each type of magnetic sensing technology focuses on a particular area for detection. The details of the sensing principle of magnetic sensor are out of the scope of this article. However, numerous literatures reported the sensing principle of magnetic sensors which can be used for the basic understanding of magnetism (Boll and Overshott, 1989; Crangle, 1989; Fraden, 2004; Jiles, 1999; Popovic, 1991; Ripka, 2001; Tumanski, 2001; Webster, 1999).

Materials for Magnetic Sensors

The predominant functional materials for magnetic sensors are semiconductors. Generally soft magnetic materials are used for magnetic sensors but hard magnetic materials are employed occasionally. In the following sections, the materials for magnetic sensors are described briefly.

Semiconductors

Semiconducting materials are used in Hall sensors (Ripka and Janosek, 2010) and magnetoresistors (Ioysher *et al.*, 1997). Traditional silicon (Si) is used for integrated Hall sensors, which are typically made by complementary metal-oxide semiconductor (CMOS) technology (Hout and Middelhoeck, 1993, 1997; Sanerman, 1984). Some other popular Hall sensor materials are carbon nanotubes (Matveev *et al.*, 2015), graphene (Dauber *et al.*, 2015; Petruk *et al.*, 2014), gallium arsenide (GaAs) (Campesato *et al.*, 1992), indium arsenide (InAs) (Behet *et al.*, 2000), indium antimonide (InSb) (Bardin *et al.*, 2017) and indium phosphide (InP) (Morvic and Betko, 2005). High-mobility semiconductors, such as InSb and InAs, have higher sensitivity compared to the other counterparts (Bardin *et al.*, 2017). The working temperatures of traditional Hall sensors range between -100°C and $+100^{\circ}\text{C}$, but some sensors work at millikelvin temperatures (Khotkevych and Bending, 2009) and others up to 400°C (Hout and Middelhoeck, 1997) whereas 4H-SiC Hall sensors may work up to 500°C (Robert *et al.*, 2002).

Soft Magnetic Materials

Crystalline, nanocrystalline, and amorphous soft magnetic alloys such as nickel-iron and nickel-cobalt alloys are used for ferromagnetic magnetoresistors. These include sensors based on anisotropic magnetoresistance (AMR) effect, giant magnetoresistance (GMR) effect, spin-dependent tunneling (SDT) effect, fluxgate effect and giant magnetoimpedance (GMI) effect (Jiles and Lo, 2003). Soft magnetic alloys are also used in flux concentrators, which are employed to enhance the sensitivity of some Hall sensors and magnetoresistors. Soft magnetic shields are used in GMR sensors. Another application is yokes for position sensors based on reluctance change. Most of the soft magnetic materials used in sensors are crystalline. Nanocrystalline soft magnetic alloys are used rarely due to their brittleness. One of the few exceptions is the nanocrystalline cores employed in current transformers. Amorphous alloys are used less often. All the mentioned materials are used in bulk form and in the form of thin films made by different deposition techniques such as sputtering, electroplating or laser deposition. Bulk materials are produced not only in the form of thin tapes but also as wires. The most common sensors based on soft magnetic alloys are AMR sensors and they are usually based on sputtered permalloy which can be used up to 225°C .

Hard Magnetic Materials

Hard magnets materials are difficult to get magnetized and for this reason they are rarely used in magnetic field sensors. If a hard magnetic material is magnetized, it will be permanent which is particularly unsuitable for magnetic field sensors. Moreover, if hard magnets are used for biasing then the involved field becomes unstable. Magnetic field sensors based on the force between the measured field and the permanent magnet are rare. More often, permanent magnets are used as a field source for position sensors. Hard ferrites and NdFeB are most often employed in these applications, but SmCo magnets are also used.

Important Parameters of Magnetic Sensors

The important parameters for magnetic sensors are sensitivity, noise, linearity, hysteresis and the temperature coefficient of the offset. Errors occur in the magnetic sensors from perming and crossfield effect which are discussed separately in the following sections.

Perming

Perming is a change of the sensor offset after the shock of a strong pulse of the magnetic field (Park *et al.*, 2004). It occurs in all sensors that contain a functional magnetic material (either as core of fluxgate or GMI sensors, as field concentrator or shields used for Hall sensors and magnetoresistors). It also occurs in other ferromagnetic parts, such as nickel-plated wires or ceramics containing magnetic particles. An efficient way to suppress the perming is periodic remagnetization of the functional magnetic parts and magnetic cleanness of the rest of the sensor.

Crossfield Effect

The crossfield effect is a nonlinear influence of the magnetic fields that are perpendicular to the sensing direction (Ripka and Billingsley, 2000). This effect appears in fluxgates and AMR sensors. A careful design of fluxgate sensors can reduce the crossfield

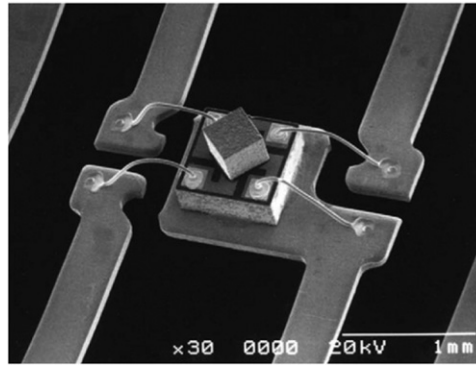


Fig. 1 Hall effect sensor based on indium antimonide (InSb). Reproduced with permission from Asahi Kasei Electronic: HW series.

error caused by the Earth's field below 1 nT. In case of AMR sensor, the crossfield error may be severe. It can be reduced by shape anisotropy, corrected by iterative algorithm. But the best way to avoid the crossfield error is to use the AMR sensor in the feedback-compensated mode.

Magnetic Field Sensors

So far, different types of magnetic field sensors such as Hall sensors, semiconducting magnetoresistors, ferromagnetic magnetoresistors, fluxgate sensors, superconducting quantum interference device (SQUID), resonant sensors, inductive magnetometers etc have been developed for various applications. In the following sections, the types of magnetic field sensors are discussed.

Hall Sensors

The Hall effects is utilized in Hall sensors. These sensors alter its output voltage in relation with the magnetic field. More than 90% of all magnetic field sensors are Hall sensors. Hall sensors are used in proximity switching, positioning, speed detection and current sensing applications (Ramsden, 2006). Most of the Hall sensors are used for position sensors (linear or angular) in automotive applications (ignition control, anti-lock braking system) and for the control of stator current in contactless DC motors with a permanent magnet rotor (from computer drives and fans up to 1 kW motors). In general, DC voltage or DC current are supplied in the Hall sensors (for basic diagram, see Fig. 1 in Permanent Magnets: Sensor Applications). However, the traditional current supply is often replaced by a voltage supply, which gives lower temperature dependence in a wide temperature range.

The key factors determining the sensitivity of Hall sensors is the electron mobility. As a result, graphene (Dauber *et al.*, 2015; Petruk *et al.*, 2014), GaAs (Campesato *et al.*, 1992), InAs (Behet *et al.*, 2000), InSb (Bardin *et al.*, 2017) and InP (Morvic and Betko, 2005) are suitable for Hall sensors due to having high electron mobility. For example, the Hall sensitivity for silicon is typically 1 mV mT⁻¹ for a 1 mA current, but a fivefold higher sensitivity is achievable using InSb (Fig. 1). Two-dimensional quantum-well multilayer structures based on InSb are promising for future applications of Hall sensors. For this, thin film of InSb are made by vacuum deposition process or molecular beam epitaxy (MBE). A proper design and using a voltage supply may reduce the temperature coefficient of sensitivity from -2%/K to $\pm 0.1\%/K$ in the temperature range of -10°C to +60°C. On the other hand, InAs sensors work in the range of automotive temperatures of -40°C to +150°C. Hall sensors with a magnetic antenna may have 10 nT resolution (Qasimi *et al.*, 2004).

Integrated Hall sensors are made on silicon, most often using CMOS technology. Example of such Hall sensor chip is shown in Fig. 2. It contains electronic circuits for the excitation, amplification and other signal processing. They may have an analog or two-state output as well as some may have digital output. The basic disadvantage of CMOS amplifiers are their large offsets. Other offsets originate from the imperfection of the Hall element itself. Effective offset reduction is achieved by rotation current technique. The symmetrical Hall element has four (or more) electrical contacts, whose role is periodically switched from current supply to voltage sensing. The switching scheme contains commutation of the polarity and thus the non-symmetry (which causes the basic offset) is averaged off.

Semiconductor Magnetoresistors

Semiconductor magnetoresistors changes its electrical resistance in response of external magnetic field. Though semiconductor magnetoresistors are less common than Hall sensors, they are still being used in the automotive industries. Modern semiconductor magnetoresistors are fabricated as a serial connection of many miniature elements on one chip. In a 100–200 mT field of a permanent magnet, such a structure may have very good temperature stability. The main disadvantage of these sensors is their

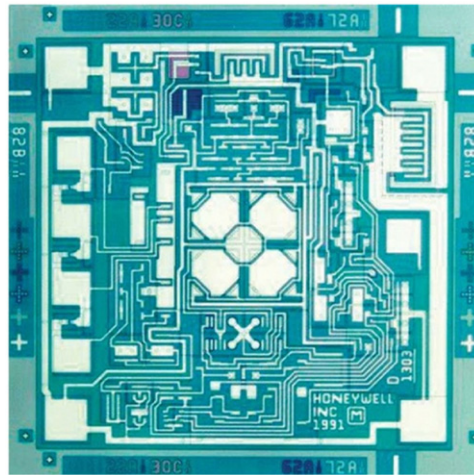


Fig. 2 Honeywell Hall bipolar IC using four cross-connected Hall elements. Courtesy of Honeywell International Inc.

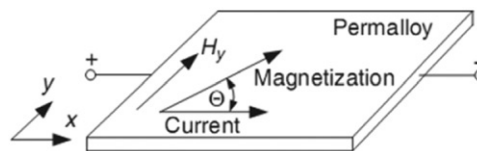


Fig. 3 Basic principle of AMR sensor. H is the measured field.

quadratic characteristics, which does not allow their use in small fields. Both magnetoresistors and Hall sensors are sensitive to the magnetic field perpendicular to the surface.

Ferromagnetic Magnetoresistors

Ferromagnetic magnetoresistors can be classified as anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR) and spin-dependent tunneling (SDT) based sensors which are discussed briefly in the following sections.

Anisotropic magnetoresistance (AMR) based sensors

Anisotropic magnetoresistance (AMR) based sensors are made of thin film (typically, 50 nm) strips of permalloy as shown in **Fig. 3**. The resistance changes about 2% with the magnetic field due to the spin-dependent scattering. The sensing direction is in the film plane, perpendicular to the strip axis. The basic AMR response is an even “hat” curve where the resistivity reaches a maximum for zero field as shown in **Fig. 4**.

Almost all AMR-based sensors adopted a “barber pole” structure: aluminum stripes sputtered on the permalloy strips deflect the direction of the current by 45° and make the characteristics linear (**Fig. 5**). Four such meander-shaped elements are connected in a Wheatstone bridge. In order to obtain the output from the bridge, the sensitivity of two branches should have reversed characteristics. This is achieved by changing the direction of the branches. AMR-based sensors were originally developed for the reading heads in hard disks, later they were replaced by giant magnetoresistance (GMR) and spin-dependent tunneling (SDT) based sensors which allow higher storage densities because of their small size. AMR-based sensors are more sensitive than Hall sensors and allow to measure with 10 nT resolution, but often require more complicated electronics which cannot be integrated on the same chip. The best AMR sensors have $200 \text{ pT Hz}^{-1/2}$ at 1 Hz noise. The proper function of AMR-based sensors relies on the complete magnetization of the magnetic layer. The sensors should be magnetized before use and this magnetization should be maintained during its lifetime. The sensor should be protected from large external fields which may change this magnetization and thus change the sensor characteristics (possibly completely reverse the response). Two forms of protection are used: bias and flipping. Biasing is used mainly in AMR position and current sensors. Biasing permanent magnet attached to AMR sensor produces field in the strip direction.

Flipping is periodical remagnetization of the structure by short pulses into the coil (which is usually integrated on the chip). Flipping is used for low-field sensors, because it also reduces the sensor offset and crossfield error. Another technique to improve the accuracy of AMR sensors is magnetic feedback, also often using the integrated coil. Feedback reduces the temperature stability of the sensor and largely improves its linearity. AMR-based magnetometers using these techniques can reach the accuracy level required for compass with 1° accuracy (Včelák *et al.*, 2005).

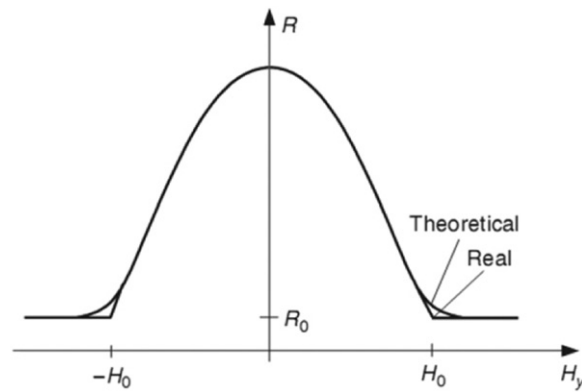


Fig. 4 Basic response curve of AMR strip.

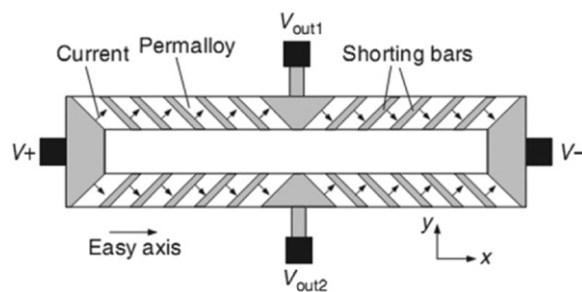


Fig. 5 Basic structure of AMR bridge with barber poles.

Giant magnetoresistance (GMR) and spin-dependent tunneling (SDT) based sensors

These sensors are made of multilayer structures. The most common GMR structure is a spin valve where two thin soft ferromagnetic layers are separated by a nonmagnetic metallic layer. In commonly used spin valves, the magnetization of one layer is fixed, while the magnetization of the other layer rotates with the external field. The resistance of such a structure depends on the angle between the two magnetizations. Also, GMR-based sensors are made in the form of Wheatstone bridges, but there is no trick similar to barber poles. The sign of response of the GMR bridge branches can be modified by DC bias. NVE use another technique: magnetically soft layer shields two branches, which become unaffected by the measured field and serve only as temperature compensation (Fig. 6). However, the latter technique leads to a nonlinear sensor with even characteristics.

The measuring current of GMR sensors flows in plane. On the other hand, in SDT based sensors, the current flows perpendicularly to the layer plane and it is tunneling through the nonconducting separation layer. Both GMR- and SDT-based sensors were developed for two-state reading heads. Much effort was made to make them suitable for linear sensing, but with only partial achievements. Therefore, up to now, they have found only a limited application, such as for counting of magnetic particles.

Fluxgate Sensors

Fluxgates are classical precise sensors developed in the 1930s. They can measure DC and low-frequency AC fields up to ca. 1 mT with a resolution of 100 pT and linearity better than 10 ppm. The measured field creates a magnetic flux in the sensor's core, which is inside the multiturn pick-up coil. This flux is modulated by using the fluxgate effect: the core is periodically switched off by saturation caused by periodical bipolar current pulses into the excitation coil. Gated flux will cause a voltage induced in the pick-up coil. The output voltage has a double excitation frequency as gating occurs twice in each period. The sensor core is made of low-noise, low-magnetostriction soft magnetic material, either crystalline permalloy or amorphous Co-based alloy.

Fluxgates are expensive, bulky, and power-consuming devices. Recent efforts have concentrated on developing miniaturized fluxgate sensors to fill the gap between fluxgate- and AMR-based sensors. Three basic paths for this development are:

- (1) CMOS-based devices with flat coils,
- (2) PCB-based devices with solenoids made by tracks and vias, and
- (3) Sensors with thin-film or microfabricated solenoids.

Cores etched from amorphous alloy (such as Vitrovac 6025 from Vacuumschmelze) are preferred as they have much better magnetic properties than thin-film cores made by sputtering, laser ablation or electroplating (Choi *et al.*, 2004; Perez *et al.*, 2004).

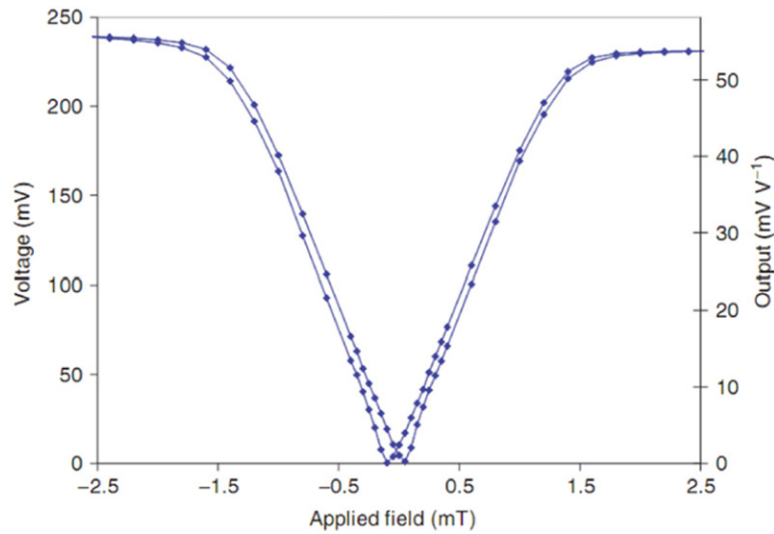


Fig. 6 Field response of bridge GMR sensor (NVE).

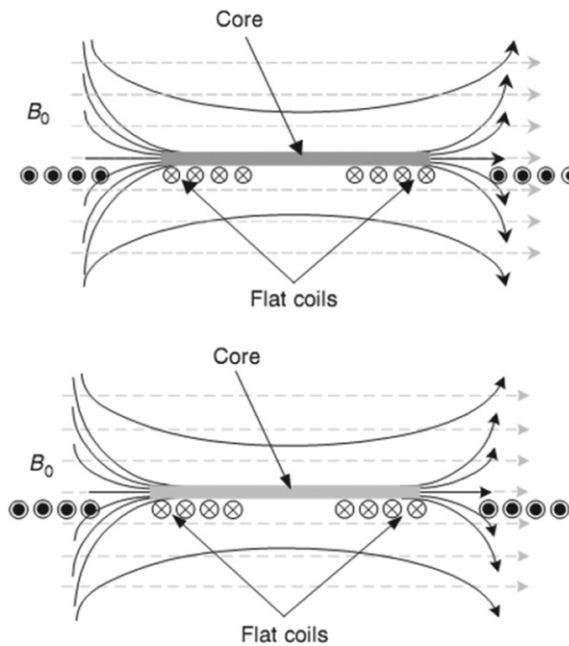


Fig. 7 Principle of flat core in fluxgate sensors.

CMOS micro-fluxgate sensors may have low-power electronics integrated on the same chip. A two-axis sensor for watch compasses can be reached $15 \text{ nT Hz}^{-1/2}$ at 1 Hz noise with 10 mW power consumption and $4 \times 4 \text{ mm}^2$ chip size (Drljaca *et al.*, 2005).

Fig. 7 shows the principle of the flat coils. Even if the coil axis is perpendicular to the core, a properly positioned coil pair can magnetize the core strip perpendicular to that axis. The challenge of this design is that the flat coil has in principle poor magnetic coupling with the core. Solenoids are much better in this aspect, but they are more difficult to manufacture. PCB-based fluxgates achieved low noise and good temperature stability (20 nT in the -20°C to $+70^\circ\text{C}$ range), but the minimum size achievable with this low-cost technology is about 10 mm (Kubik *et al.*, 2006). Smaller solenoids can be made by thin film technology (Joisten *et al.*, 2005). Besides the mainstream, a lot of modified fluxgate sensors have appeared. One of them is based on the transverse fluxgate effect, which may find application in miniature sensors.

Superconducting Quantum Interference Device (SQUID)

Superconducting quantum interference device (SQUID) magnetometers are based on superconducting Josephson junction and flux antenna. These extremely sensitive devices measure magnetic field changes rather than absolute field value. Low-temperature (LT) SQUIDs work at liquid helium and they have 1 fT field resolution. High-temperature (HT) SQUIDs work at liquid nitrogen and have about 50 fT resolution. Such a high sensitivity does not allow direct operation, as the sensor would be overloaded by the Earth's field. Thus, the gradient coils and magnetic shielding should be used. SQUIDs are at present used for biomagnetic experiments and for measurement of magnetic properties of samples that are small or magnetically very weak.

Resonant Sensors and Magnetometers

Unlike all the other magnetic sensors, resonant sensors measure the total field value (scalar) rather than its vector. This means that the reading is not dependent on the field direction (with the exception of possible dead zones). This may be an advantage in cases when the directional information is not required or it can be derived using other sensors. In such cases, the field measurement is easy, as the direction of the sensor head is arbitrary. The main advantage of resonant magnetometers is that they are absolute instruments with very small uncertainty. Resonant magnetometers coupled to three-axial fluxgates are popular combinations to achieve long-term stability of the vector magnetometer. The disadvantage of resonant magnetometers is that they usually have limited field range and they fail at low fields.

Proton magnetometers

These devices are based on the gyromagnetic effect. The volume of a liquid is polarized by a strong magnetic field. After the polarization field is switched off, magnetic moments move toward the direction of the measured field B . During this transit, the molecules (like mechanical gyroscopes) exhibit precession with an angular frequency of $\omega = \gamma B$, where γ is gyromagnetic ratio of the proton. The corresponding frequency constant is 42 MHz T⁻¹, which means that 1 nT change corresponds to only 42 mHz frequency change. Classical proton magnetometers are sensitive to field gradients and interferences and thus they generally cannot be used in buildings. They require relatively large sensor volume (10–500 ml) in order to pick measurable signal.

Overhauser magnetometers

The Overhauser effect (dynamic nuclear polarization) is a transfer of energy from large electron magnetic moments to protons in the same sample. Electrons from free radicals in the sample are continuously excited by 60 MHz RF field. In this way, protons can be polarized easier than using DC magnetic field. Free precession frequency of the protons can be observed after the RF signal is switched off, but the instrument can also work in a continuous mode. Overhauser magnetometers are more resistant to field gradients than classical proton magnetometers and they also measure faster. The instrument can have 0.1 nT resolution and 0.5 nT absolute accuracy.

Optically pumped resonance magnetometers

These devices are based on the Zeeman splitting of electron energy levels, which is proportional to the magnetic field. Cesium vapor in the resonance cell is excited by monochromatic light (from a discharge lamp that is also filled by cesium vapors). Thus the photons have just the right energy to excite the electrons into a higher orbit and the cell has the maximum absorption of light. But this happens only in zero magnetic field. If a field is present, the associated Zeeman splitting creates new energy levels, from which the electrons cannot be excited by the monochromatic light. After some time, all electrons stay at these new ($m = \pm 1$) levels and the cell becomes transparent. By applying AC field with appropriate frequency, electrons are excited from the new $m = \pm 1$ levels to the basic $m = 0$ level, from which they can be again light-excited. The frequency of the AC field depends on the measured DC field.

Induction Magnetometers

These devices are based on the Faraday induction law, which means that the voltage sensitivity is proportional to the frequency. In order to obtain flat frequency characteristics, one can use an integrator at their output. Another possibility is to use a current output. Current-output induction coils have flat frequency characteristics for frequencies larger than $R/2\pi L$. Induction coils are used for AC magnetic fields in the frequency range of 110 mHz to 1 MHz. At low frequencies, ferromagnetic cores are used to increase the sensitivity. The optimum shape of such core is a long rod and the coils are slim solenoids (Seran and Fergeau, 2005). For higher frequencies, air cores are used, and the optimum shape of the coil is large loop.

Other Devices

The giant magnetoimpedance (GMI) effect is based on the field-dependent change of the penetration depth. The effect has only few practical applications as it gives weak, temperature-dependent signals and the characteristics are nonlinear and unipolar. Asymmetric GMI sensors give linear responses, but the effect is based on potentially unstable self-biasing (Knobel *et al.*, 2003).

Table 1 Basic properties of precise magnetic sensors

Principle	Sensor	Size (mm)	Noise (pT/ $\sqrt{\text{Hz}}$ @1Hz)	Power (mW)	Reference
Fluxgate	Ring core	25	3.8	50	(Ripka, 2003)
	Ring track	70	2.5	70	(Ripka, 2003)
	PCB	30 × 8 × 1.8	17	20 (pulse exc.)	(Kubik <i>et al.</i> , 2006)
			13	50 (sine exc.)	
	Thin Film	3 × 3	1000	10 (100 ^a)	(Joisten <i>et al.</i> , 2005)
AMR	CMOS micro	1.5 (4 × 4 ^a)	15,000	(10 ^a)	(Drljaca <i>et al.</i> , 2005)
	HMC 1001	4 × 11 × 1.7	200	30 (5 V, 0.86 k Ω)	(Zimmermann <i>et al.</i> , 2005)
			300	1.7 (1.2 V, 0.86 k Ω)	(Stutzke <i>et al.</i> , 2005)
	HMC 1023 ^b	8 × 4 × 4	1000	30 (each axis)	(Zimmermann <i>et al.</i> , 2005)
	HMC 1021 \$ \$	4 × 5 × 1.7	3000	1.5 (1.2 V, 1 k Ω)	(Stutzke <i>et al.</i> , 2005)
	KMZ 51	5 × 4 × 1.7	2000	15	(Zimmermann <i>et al.</i> , 2005)
			1600	15 (5 V, 1.7 k Ω)	(Vopalensky <i>et al.</i> , 2003)
	+ Flipping	–	–	25 mW/1kHz	–

^aIncluding electronics.^bThree axis.

Another effect with questionable potential for magnetic sensing is the colossal magnetoresistance. Magnetostatic devices (Ciudad *et al.*, 2004) and magneto-optical sensors based on Faraday effect may be used to measure very large fields.

Magnetotransistors and magnetodiodes are rather exotic devices, which periodically appear in literature, but do not show any advantage over simple Hall sensors. In Table 1 an overview of low-noise magnetic field sensors are presented.

Magnetic Position and Distance Sensor

The magnetic position and distance sensors can be divided into linear variable differential transformer, inductosyn, synchros and resolvers, Eddy current sensors, variable reluctance sensors, magnetic encoders, permanent magnet linear contactless displacement sensors (PLCD) and magnetostrictive position sensors. The types of magnetic position and distance sensor are discussed briefly in the following sections.

Linear Variable Differential Transformer (LVDT)

Linear variable differential transformers (LVDTs) are differential transformer devices that have movable cores (Fig. 8). The primary winding is supplied from the voltage source and the voltages on two symmetrical secondary windings are monitored. If the core is displaced from the central position, one secondary voltage is larger. LVDTs are one of the most popular position sensors. They are available in measurement ranges from 200 μm to 50 cm, the resolution is from 1 μm , and linearity up to 0.05%.

Inductosyn

Inductosyn is a position-sensitive transformer with movable flat meander coils. It combines an analog output (within one coil pitch) and incremental output (counting of pitch numbers). Inductosyns are often used in large machine tools. Beside this, due to having ruggedness inductosyn sensors are being used in military and aerospace applications. The standard linear accuracy is 1 μm or 1" for rotary type.

Synchros and Resolvers

Synchros and Resolvers devices are rugged rotational transformers which are similar to electric machines. Their typical application is in heavy industry and military systems.

Eddy Current Sensors

Eddy current sensors allow to measure the distance of the conducting target, which need not be a part of the sensor. If the excitation frequency is large enough so that penetration depth is very small, the reading does not depend on target width and its conductivity. Most of the proximity switches are based on this principle. The basic circuit consists of an LC oscillator, which is "killed" by losses due to the eddy currents.

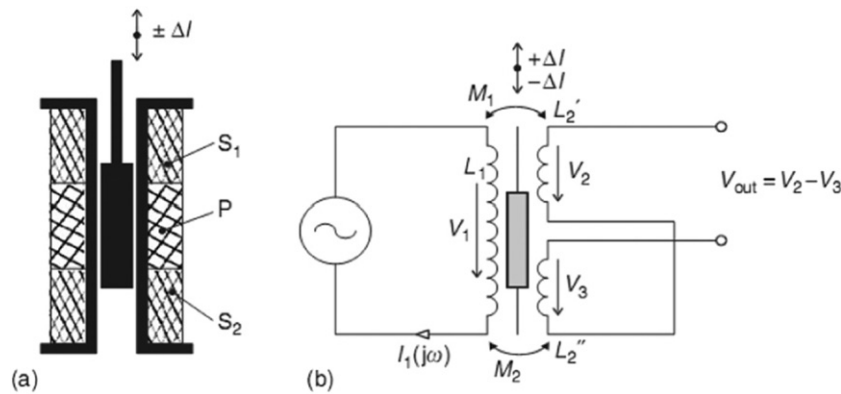


Fig. 8 Linear variable differential transformer (LVDT) position sensor.

Variable Reluctance Sensors

Variable reluctance sensors measure the changes of the air gap in a magnetic circuit. They need AC excitation and can be made as transformers or variable inductors. Differential sensors of this type have improved linearity.

Magnetic Encoders

Magnetic encoders are available as incremental or absolute position sensors either in linear or rotational form. They use magnetic marks created in ruler or wheels made of hard magnetic material. Absolute magnetic encoders need multiple tracks and associated sensors. Rotational magnetic encoders may have up to 10 bit resolution.

Permanent Magnet Linear Contactless Displacement Sensors (PLCD)

Permanent magnet linear contactless displacement sensors (PLCDs) use a soft magnetic core, which is saturated in one point by a permanent magnet attached to the target. The primary winding of a differential transformer is wound over the entire core length and two secondary coils are at the core ends. The saturated region magnetically divides the core into the two separated parts. The coupling between the primary winding and each of the secondary windings depends on the length of these two parts. They were developed for automotive and industrial applications, which do not need high precision, but robustness and contactless operation over a large air gap.

Magnetostrictive Position Sensors

Magnetostrictive position sensors use sonic waveguides made of magnetostrictive wires or tubes. When a movable permanent magnet saturates a small region of such a waveguide, the traveling strain pulse is partly reflected from this region back to the source. The time-of-flight is then proportional to the distance between the source and magnet. Another reflection from the waveguide end is also measured and used to compensate for the sound velocity, which is temperature dependent.

The length of these sensors is limited by attenuation to about 4–6 m. Resolution can be as low as 0.4 μm and uncorrected nonlinearity 0.02% FS. Magnetostrictive delay lines allow to measure also other physical variables at multiple points (Hristoforou, 2003).

Magnetic Proximity Switches

Proximity switches can be made from any distance sensor and Schmidt trigger. Hall sensors with permanent magnets and eddy current sensors are often used in this form. The following two magnetic sensors give natural bipolar outputs: magnetic reeds and Wiegand wire.

Reed Contact

Reed contacts are cheap and robust and need no power. They are based on attractive force between two soft magnetic strips, which are magnetized by a permanent magnet. Both normally open and closed contacts are available. The position of the moving permanent magnet should be selected carefully to avoid multiple switching regions.

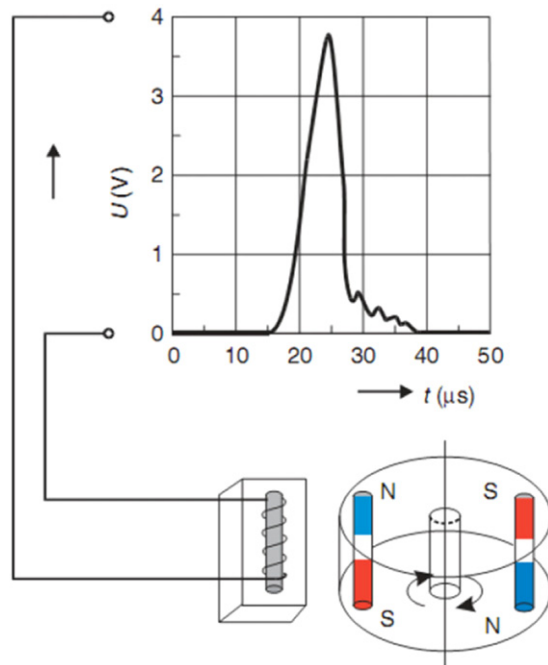


Fig. 9 Wiegand wire.

Wiegand Wires

These sensors are also called “pulse wires”. They are based on the asymmetric hysteresis loop of the composite material and a large Barkhausen jump. The characteristics is biased either by a piece of permanent magnet in the form of a parallel wire or by an external magnetically hard layer on the same wire. As a result, the large Barkhausen jump appears only on one side of the loop.

These sensors produce a voltage pulse, which is to some extent independent of the speed of the moving permanent magnet (Fig. 9). The advantage is that the sensor needs no power. A disadvantage is that it can be destroyed by strong magnetic fields.

Other Magnetic Sensors

Several other types of sensors such as magnetic force and torque sensors, magnetic flowmeters, current sensors are discussed briefly in the following sections.

Magnetic Force and Torque Sensors

Many force and pressure sensors use deformable elastic elements together with a magnetic position sensor. Magnetic load cells (pressductors or torductors) are based on a transformer with perpendicular windings. In the unloaded state, the coupling between the primary and secondary winding is zero and there is no output voltage. In the loaded state, the stress-induced anisotropy causes asymmetry of the flux lines and an output voltage appears. Torque sensors are also based on stress-induced anisotropy. The torque on the rotating shaft can be measured without contact by external coils.

Magnetic Flowmeters

Magnetic flowmeters use electric fields created in conductive liquid flowing in a magnetic field. The field is usually a square wave created by saddle coils around the pipe. The electric field is commonly detected by the voltage between the two conducting electrodes in the liquid, but it can also be measured without contact by two electrodes on the outer surface of the nonconducting pipe.

Current Sensors

Almost all contactless current sensors use a magnetic principle (Ripka, 2004). Current sensors can be divided into instrument current transformers, Rogowski coil, DC current transformers, Hall current sensors and AMR current sensors. The types of current sensors are discussed in the following sections.

Instrument current transformers

Precise current transformers use high-permeability ring cores to scale down the measured current and convert it to voltage drop on load resistor. They are also made with an openable core, most often as AC current clamps. Current transformers were used in electronic energy meters, but it turned out that they could easily be disabled by a saturation, either from strong permanent magnets or from the DC component in the measured current. One way to avoid this is to use a flat-loop magnetic material, which has a very high saturation field H . Another approach is to use Rogowski coil, which has no magnetic core.

Rogowski coil

Rogowski coils for measurements of currents are wound around the measured current conductor. They measure dI/dt . Normally they are used together with an integrator. Single-chip digital integrators are used to process the signal of Rogowski coils (also called dI/dt sensors) for energy meters.

DC current transformers

Basic current transformers use only AC currents. DC current transformers (or DC current comparators) use the fluxgate effect in cores which are periodically saturated by excitation field.

Hall current sensors

Many DC current sensors use a Hall element mounted in the air gap of a magnetic core. The sensor linearity can be increased by the feedback principle. The multiturn feedback coil allows a feedback current much lower than the measured current.

AMR current sensors

AMR sensors are more sensitive and stable than Hall sensors, but they cannot be used in the narrow air gap of the magnetic core, as they measure field in the sensor plane and usually require more than 1 mm sensor length in the field direction. Such large air gap would cause field leakage and result in sensor nonlinearity and sensitivity to outside a magnetic field. Current sensors are based on AMR magnetoresistors and thus are yokeless. They use two geometries:

- (1) A bridge measuring the magnetic gradient from the current (Fig. 10) and
- (2) A multisensor arrangement in a circular pattern around the measured conductor.

The first type geometry uses a current conductor integrated with the sensors in a given device and it is suitable to measure currents up to 40 A. The second configuration is used to measure very large currents.

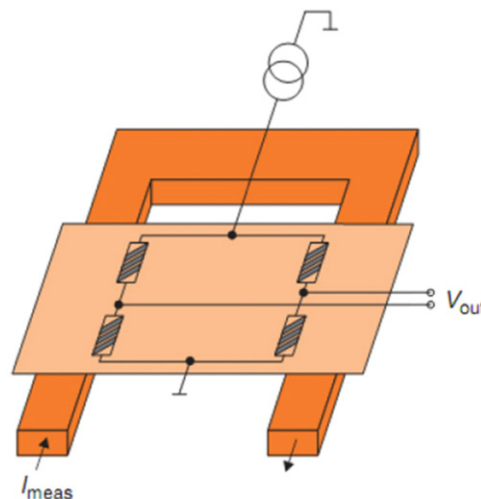


Fig. 10 Configuration of an AMR current sensor.

Applications of Magnetic Sensors

Magnetic position sensors are cheap and robust. They can work in dirty environments (e.g., under an oil film), where optical sensors fail. The magnetic proximity switch is probably globally the most-used sensor type. Some of the important applications of magnetic sensors are discussed in the following sections.

Position Measurement

Position measurements are the main application of magnetic sensors. The advantages of magnetic sensors are low cost and ruggedness. Rotational speed and position sensors are used in automotive industry (e.g., for ignition timing and anti-lock braking system). They are most often based on a Hall sensor integrated with a small permanent magnet. A ferromagnetic toothed wheel changes the magnetic path for the magnet, and thus, for a rotating wheel, the Hall sensor observes a changing field. AMR sensors start to penetrate this market; due to their higher sensitivity, they allow one to use larger air gaps between the sensor and the wheel.

Position Tracking

Magnetic position trackers use multi-axial artificial magnetic field created by a coil system. Three-axial magnetic sensors (usually induction coils, AMR sensors or fluxgates) are attached to the tracked object. Trackers are used in virtual reality and entertainment, but they also have many industrial applications. One example is the drilling and mining industry, where trackers measure the distance and position between drilling paths and underground tunnels. Sophisticated techniques are used to detect and correct field distortion caused by metal objects.

Navigation

The traditional magnetic compass has the moving needle leveled in horizontal plane. It is possible to detect the position of this needle by Hall sensors; however, this is very inaccurate. Precise electronic magnetic compasses traditionally use fluxgate sensors and they reach 0.1° accuracy. Keeping sensors in the horizontal plane is not practical, especially for fast moving platforms. In this case, it is possible to use tri-axial magnetic sensors and two inclinometers, and recalculate the correct azimuthal angle from the known pitch and roll. This is called a strap-down compass. AMR sensors give less precision. The main source of error is here the crossfield. Fig. 11 shows the corresponding azimuthal error. After all the corrections, 1° azimuth error is typical for an AMR compass, but it is sufficient for many portable applications, as the compass is usually used together with Global Positioning System (GPS) and the earth's field is often distorted by ferromagnetic bodies anyway.

Antitheft Systems

Antitheft systems use permanent magnets or other targets attached to the monitored objects. The most popular are magnetostrictive targets where the strip of magnetostrictive material has a high absorption of an AC magnetic field at its mechanical resonance frequency. The label can be deactivated by a magnetic field.

Detection of Vehicles

Magnetic sensors (fluxgates and AMRs) are used to detect and recognize vehicles. This is used for traffic control and for security and military purposes (Kang *et al.*, 2005).

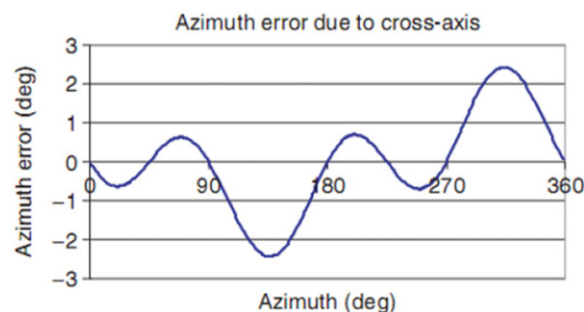


Fig. 11 Azimuth error of AMR compass caused by crossfield effect.

Location of Unexploded Ordnance (UXO) and Mines

Detectors for antipersonnel mines use eddy currents in conductive targets. The detector head is a flat coil, often with a gradient. Continuous types work typically at 10 kHz frequency, pulse types sample in 35–80 μ s time after the abrupt change of large current step. These detectors are optimized to find low-metal content mines in small depths. There are two main problems of mine detectors: high false-alarm rate and signals from magnetic soils. The latest models combine an eddy current method with ground-penetrating radar (GPR), which allows one to observe the shape of the nonmetallic part of the mine using its contrast in susceptibility. Modern detectors can compensate magnetic soils, but problems occur when the soil has superparamagnetic nanoparticles, which exhibit magnetic viscosity, that is, frequency dependence of susceptibility or noninstant response to the field step. Detectors for large and deeper objects (antitank mines, bombs, and unexploded ordnance (UXO)) use similar principles, but with much larger loops, or they are based on DC magnetic gradiometers. Magnetometers can detect large bombs as deep as 6 m. They either measure the vertical gradient using two fluxgates, or the scalar vertical gradient using two Overhauser or cesium-type magnetometers. An extremely precise triaxial fluxgate gradiometer is described by (Merayo *et al.*, 2005).

Space Research and Geophysics

Space DC magnetometers use three orthogonally mounted fluxgate sensors together with a resonant magnetometer (Acuna, 2002). Satellites with a scientific magnetometer on board should be made from carefully selected, if possible, nonmagnetic materials, and the magnetometer should be mounted far from the satellite body so that the fields from the satellite itself are sufficiently small. AC fields are usually measured by iron-cored induction coils. Geophysical and archeological prospecting methods include DC magnetometry and measurement of magnetic properties of samples. The remanent magnetization is frozen when the sample passes through the Curie temperature. As the historical drift of magnetic poles is known, when the sample orientation is documented, the remanent magnetization can be used for dating of archeological (bricks) or rock samples.

Medical Distance and Position Sensors

Magnetic trackers are used to navigate catheters inside the body. 1 mm precision is achievable for 2 mm diameter sensors. The main operational principle is a simple wire-wound induction coil. As the body liquids are highly conductive, the field frequency should be small, typically 1 kHz.

Magnetic biscuits are used to monitor the digestion tract. These biscuits are swallowed and their movement is monitored by external magnetic sensors. They are based on the same technologies as magnetic trackers with passive marker, which may be hard magnets, soft magnetic materials, Wiegand wires, LC resonators, or RF transponders.

Magnetic Labeling and Detection Using Microparticles

Superparamagnetic magnetic particles are ideal labels for biosensing. They can be manipulated by a field gradient and detected by field sensors. GMR and especially SDT sensors are suitable for this application because of their small size. The nonlinearity of these sensors does not matter in such counting application.

Nondestructive Testing

Magnetic nondestructive testing (NDT) and evaluation methods include DC and AC tests (Butin *et al.*, 2005; Vertesy and Gasparics, 2003). DC flux leakage method is used to find cracks in ferromagnetic parts and also to detect corrosion in pipelines. These methods use fluxgate sensors or magnetoresistors as magnetic field detectors or the field is visualized using ferrofluids, that is, liquids that contain colloid ferromagnetic particles.

AC methods based on eddy currents can be used for every conducting part. Cracks or other discontinuities cause changes in the eddy current path, which results in an impedance change of the testing coil (or in the amplitude of the induced voltage). Magneto-optic methods allow noncontact evaluation (Lee *et al.*, 2005).

Summary

Magnetic sensors are used to detect magnetic fields and they are essential tool for many engineering applications. Based on the applications, many variations of magnetic sensors have developed which can be classified in few groups: magnetic field sensors, magnetic position and distance sensors, magnetic proximity switches, magnetic force and torque sensors, magnetic flowmeters and current sensors. Each of the class has many variations of sensors. Magnetic sensors are being used in almost all engineering applications such as automobiles, military, robotics, medical devices, space equipment, geophysics and industrial measurements.

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Conducting Polymer Based Sensor

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Abstract

Polymer materials are traditionally perceived as insulating materials before the advent of organic π -conjugated polymers. These electrically conducting polymers have generated considerable interest due to their flexibility, corrosion resistance, light weight, low cost and excellent optical, electrical and mechanical properties. Among the myriad of applications for these materials, fabrication of sensors is given significant attention. Conducting polymers offer multiple technological solution to sensor manufacturing. Polymers can serve as either active sensor element or support to sensing units. Their chemical structure can be easily and significantly modulated to achieve desired reactivity, selectivity, biocompatibility and degradation resistance. This chapter discusses the advantages of conducting polymer sensors, their application and strategies adopted to improve their sensing response.

Key Points

- Conducting polymers for sensing application is analysed.
- Synthetic strategies employed for developing polymeric material as sensors are discussed.
- Modes of sensing and various applications of polymer sensors are elaborated.
- Merits and demerits of the devices are discussed based on the stability, quantification, detection limit, sensitivity and quantification limit.

Introduction

From the last few decades, development in the field of sensors has increased exponentially in terms of active researchers, published literature and financial investments (Kar *et al.*, 2015). It is notable that the capacity of a sensor is to give data on our physical, biological and chemical environment. Various Govt agencies have fostered vast demand for sensors in monitoring of environmental contaminants in water bodies either by industrial effluents or from agricultural fields (Piroozmand *et al.*, 2020). In this way, a close to transformation is evident in sensor research, bringing forth an enormous number of sensor gadgets for environmental and clinical technology (Saccomano *et al.*, 2021). A common chemical sensor reveals information or data about its environment and typically consists of a selective later and a physical transducer (Naresh and Lee, 2021). Sensors based on biological materials called biosensors contain a biological moiety such as cell tissue, bacteria, antibody or enzyme as recognition element (Mehrotra, 2016). Most of the sensor devices have been fabricated from insulators, catalytic materials, classical semiconductors, metals and solid electrolytes (Das and Prusty, 2012; Rajesh *et al.*, 2009). Polymer-based science has prompted a totally new group of sensor devices and materials utilising polymers which present the capacity to show a certain response when comes in contact with analyte (Fig. 1). The response relay or in recognition of the target species by receptors motifs is by selective interaction following the transduction process which originates by a small measurable change (Alberti *et al.*, 2021). In addition, polymeric based sensors are easily moulded into various shapes such as wires, coatings, beads, films, microfibers etc (Ruiz *et al.*, 2018).

Since the physical and chemical properties of the polymeric compounds may be tailored in gaining interest for the development of sensor devices as they are having good insulating properties (Spychalska *et al.*, 2020). Most of the recent studies reveals that most of the polymeric compounds acquire a key spot as device materials as compared to other materials (Sikder *et al.*, 2021; Song *et al.*, 2018). Previously, materials used for polymer-based sensors include Poly(3,4-ethylenedioxythiophene) (PEDOT), polythiophene (PTh), polyaniline (PANI), and polypyrrole (PPy). All these materials have been at the forefront for polymeric based sensors for decades because of their specific properties (Yoon, 2013). Polymers based sensors have many advantages such as low cost, light weight, resistance to corrosion, processability, and excellent optical mechanical and electrical properties. Use of polymeric material in sensing not only improves the recognition of the target molecules but also supports the immobilisation of the different functionalities such as metal nanoparticles, dyes, fluorophores etc. They detect the target analyte by changing their chemical or physical characteristics (Cichosz *et al.*, 2018). The major advantage of using polymer materials in sensors is the possibility of modifying their resistance to degradation, chemical properties, biocompatibility, tuning their reactivity and flexibility (Sanjuán *et al.*, 2018).

The chemical stability of the polymeric material for sensing makes them ideal for detecting volatile organic compounds, toxic gases and other such as chemical anions, humidity, alcohol etc. Polymeric based materials in biosensors are used to detect different

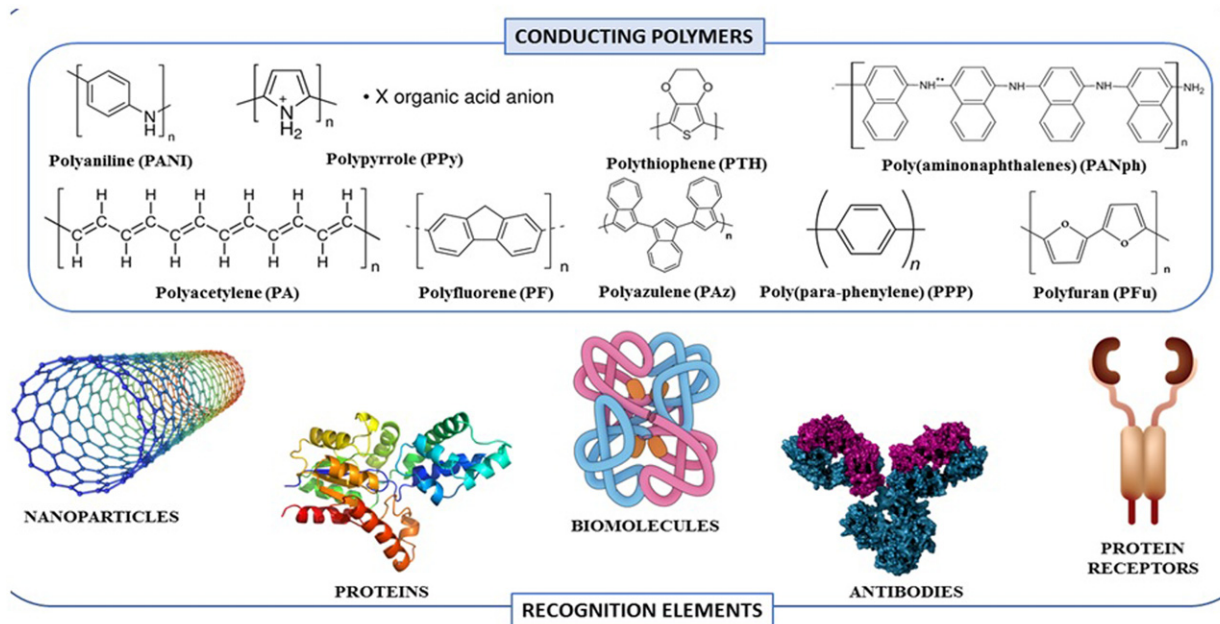


Fig. 1 Conducting polymers and various recognition elements incorporated in them for sensing application.

ranges of biomolecules compounds such as proteins, nucleic acid, antibodies, enzymes etc (Vigneshvar *et al.*, 2016). This book chapter examines the different synthetic strategies for using polymeric material as sensors, different modes of sensors and its applications. Efforts have also been made to incorporate various challenges while designing a polymeric based sensor. For each section, we focused on highlighting the merits and demerits of the devices according to their stability, quantification, detection limit, sensitivity and quantification limit.

Conducting Polymers as Sensors

Traditionally polymers were distinguished as insulating materials. They are easily processable, economical and light weight. Corrosion resistance of polymers makes them suitable for long term applications. The pioneering work by Heeger, MacDiarmid and Shirakawa established the field of conducting polymers (CPs). These polymers possess a conjugated backbone of alternating double and single bond which impart intrinsic electrical conductivity. The electron dense π bonds, which are highly delocalised, are responsible for optical and electrical properties of these conducting polymers. Mode of charge propagation in CPs is correlated to their chemical structure. Charge propagation happens either through electron delocalisation in conjugated systems or through electron hopping between neighbouring redox sites (Tomczykowa and Plonska-Brzezinska, 2019). Conducting polymers can be categorised into three depending on their chemical properties: (i) amphoteric polymers which can undergo redox reaction to generate polycarbanion or polycarbo cations, (ii) polymers with neutral chains which can only be oxidised to form polycarbo cations and (iii) polymers having strong basic centres which can react with protonic acids to forming adducts (Magu *et al.*, 2019).

Conjugated polymers have been synthesised by various methods including chemical oxidation, electrochemical polymerisation, catalytic polymerisation, vapour phase synthesis, solvothermal, hydrothermal and photochemical methods. Compared to conventional polymers, CPs contain lower number of monomer units. Typical conducting polymers include polyaniline (PANI), polypyrrole (PPy), polyacetylene (PA), polythiophene (PTH), polyfluorenes (PF), polyazulenes (PAz), poly(aminonaphthalenes) (PANph), poly(para-phenylene) (PPP), polyfurans (PFu) and their derivatives. Conjugated polymers were originally explored as substitutes to metals. Their properties can be easily modulated through surface functionalisations, structural modifications and doping, making them versatile candidates for various niche applications. Over the past 20 years their scope of potential has diversified into fields like energy storage/conversion (Kausar, 2017; Wang *et al.*, 2017), electrocatalysis (Lahiri *et al.*, 2020; Tang *et al.*, 2020) and sensing (Moon *et al.*, 2018). In addition, polymer materials have been found have good biocompatibility making them suitable for biosensing applications in the healthcare sector.

Conducting polymers offer diverse technological solutions for developing sensor materials. Technological advancement in polymer synthesis, fabrication and modification methods have added effective features into conducting polymers making them smart materials for sensor applications (Gillies, 2020). Conjugated polymer sensors are observed to be highly sensitive and selective towards analytes. The high sensitivity of the conjugated polymers originates from the sensory signal amplification which is attributed to energy migration along the polymer backbone upon analyte interaction (Nair *et al.*, 2019). The conjugated backbone of the conducting polymer transfers the information of analyte binding to neighbouring sensing units, thereby

enhancing the signalling response. This effect is widely used in fluorescence detection of analytes like explosives, inorganic ions etc. This 'molecular wire effect' effectively quenches/enhances the fluorescence of the polymer leading to higher sensitivities. Amplified sensing is also observed by coupling a donor conjugated polymer with a small acceptor chromophore.

Conjugated polymers have been designed to sense a wide range of analytes under ambient conditions. The inherent electron or energy transport properties of the polymer readily generates response upon interaction with analyte. Polymer structure can be altered by synthesis and fabrication methods to control selectivity towards a specific target analyte. Besides, sensitivity can be controlled by synthetic means, integrating more sensing moieties. Polymer sensor arrays have been prepared by various fabrication methods, extending their application in multianalyte detection (Li *et al.*, 2018; Micolini *et al.*, 2017).

CPs have been employed in catalytic and affinity sensors as analyte recognition elements, matrix materials for immobilisation of active centres and even as signal transducers. Selection of appropriate monomer unit is critical for the formation of analyte recognition element in conducting polymers. Various methods utilised for incorporation of recognition element onto the conducting polymer chain is discussed in the upcoming section. Composites of conducting polymer and recognition elements like nanoparticles, enzymes, DNA, antibodies and receptor like proteins have been reported for sensors (Naveen *et al.*, 2017). In such cases, CPs perform the dual function, as a matrix for active material as well as transducing element for signal transduction.

CPs as a sensor layer can generate different types of responses upon exposure to analyte. The electronic and optical properties of the polymer get altered by varying doping levels. Chemical interaction with analytes can affect the doping levels even at room temperature. This serves as a simple technique in sensing of analytes. Doping/de-doping redox reactions involve electron transfer between polymer and analyte. Electron accepting analytes remove electron from aromatic rings whereas electron donating analytes inject electrons to the polymer chain. This results in altering of intrinsic conductivity which can be measured as a change in resistance for electrical/electrochemical sensors (Alqami *et al.*, 2020) or as optical response in optical chemical sensors (Gicevičius *et al.*, 2017). Electrical sensors like field effect transistors (FETs), chemiresistors, capacitive sensors have been reported to be fabricated from conducting polymers. Optical sensors are subdivided into colorimetric, ratiometric and fluorescence sensors. Conducting polymers can also detect inert analytes that otherwise do not react under ambient conditions. Weak interactions of these analytes can induce physical changes like modification of backbone conformation and swelling of the polymer matrix. These interactions do not affect the oxidation state of the polymer. However, they alter the electron mobility or delocalisation and generate electrical or mechanical signals. These adsorption-based sensing is widely applicable to volatile organic compounds and similar small molecular systems which can get adsorbed in the polymer matrix.

Synthesis Strategies for Polymer Sensors

In a conjugated polymer-based sensor the sensing is achieved by introducing a molecular recognition moiety that has an affinity towards specific analytes. It can be done either by structural modifications or by embedding sensing materials in the matrix. In structural modification method, sensing moiety on a polymer is incorporated either within the backbone or as a side chain. These modifications are performed either to the monomer units prior to polymerisation or through post-synthesis modification of the polymer. The sequence and structure of the polymers can be effectively modified to suit the requirement of diverse target analytes by introducing different functional groups. The functional groups define the electronic and steric properties of the polymer at the molecular level and direct the interaction with analyte. This section discusses several methods used to incorporate sensing element into the polymer.

Sensing Element on Polymer Backbone

The inclusion of active sites in the polymer backbone is one of the simplest strategies to prepare sensors. C-C coupling reactions like Sonogashira, Suzuki, Heck, oxidative polymerisation, electropolymerisation are utilised to combine multiple aromatic monomers for tuning the physical properties and sensing behaviour. Monomers with specific functional groups are designed to selectively interact with target analyte(s).

The use of 1,3,5 oxadiazole based linear polymer with 2,2' bipyridyl group for the detection of metal ions (Fe^{2+} and Cu^{2+}) by using bipyridyl ring as coordination site has been reported (Kim *et al.*, 2010). An other polymer such as 2,6-dithienyl-4-phenylpyridine (TPP) was also developed by copolymerisation with 1,4-diethynyl-2,5-(bis(hexyloxy) benzene as the metal sensing unit for the detection of Pd^{2+} using colorimetric approach and the detection limit was found to be 10^{-6} M (Liu *et al.*, 2011). π conjugated donor acceptor polymers are also excellent candidates for metal ion sensing. The coordination of metal ion affects the charge transfer properties of the native polymer resulting in fluorescence quenching. A series of polymers using carbazole as hole transfer unit and 2,3-dimethylquinoxaline as electron transfer and luminescent unit was also reported which produces fluorescence quenching upon addition of Ni^{2+} (Upadhyay and Karpagam, 2017). In these systems, the orientation of the coordinating site is severely affected by the polymer chain stiffness and hence there is much less control over the size of coordinating sites. The intra-chain aggregation forming coordination pockets is also restricted by the bulky side chains which are added to improve solubility.

Sensing Element on Polymer Side Chain

The inclusion of active site on the side chain or as pendant group opens up new possibilities in designing sensors. Well known chelating groups or even cyclic moieties can be appended onto the polymer chain, giving better control over the size and geometry of the

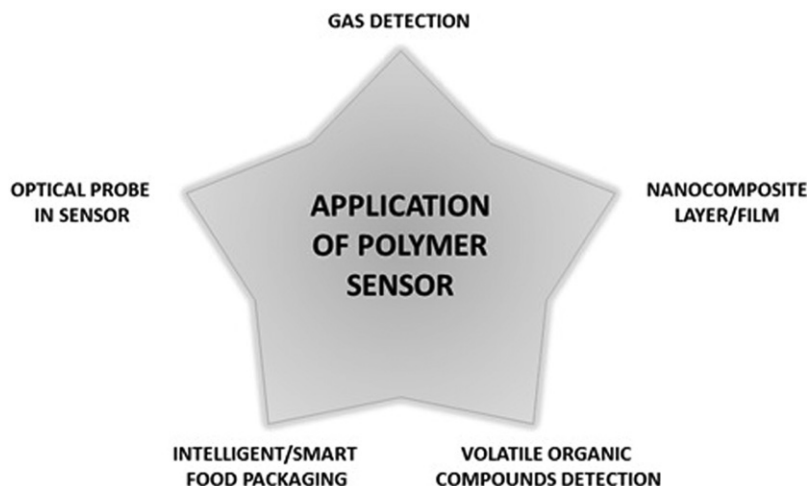


Fig. 2 Different applications of polymer sensors.

coordinating centre. The effect of side chain on the selectivity of a conjugated polymer is reported by *Kang et al. (2021)*. Field effect transistor (FET) sensor for NO_2 showed exceptional improvement in selectivity when the same conjugated framework was modified by different flexible side chains. Structure driven morphology of the polymer systems modified the charge carrier properties and improved the affinity towards NO_2 . In a similar study, tuning pendant groups on polythiophene was demonstrated to show discriminate responses to volatile organic compounds (VOCs) (*Tu et al., 2017*). Chemiresistor sensor arrays were prepared by varying the concentration of triethylamine and 1-methyl imidazole pendant groups for VOC classification. Appropriate pendant group modifications generate preferential interaction with VOCs. The combination of different pendant group containing polymer systems enabled capturing and assaying wide range of VOCs. Conjugated polymers with terpyridyl, fluorenes, phenylene and benzimidazolyl-pyridine ligands attached to phenylene via hexamethylene spacer were also synthesised having the ability to form complexes with Zn^{2+} and Cu^{2+} and changes colour after addition of metals (*Bao et al., 2013*; *Sil et al., 2018*; *Wang et al., 2020*). Fluorescent molecules or quenchers are attached to the side chain inducing resonance energy transfer which is utilised for sensing. These side chain substitutions can simultaneously act as energy acceptors and reaction centres for analyte interaction (*Wang et al., 2015*).

Post-Synthesis Modification

Post-synthesis modifications append the sensing element to a conjugated polymer system after its synthesis. Different post synthesis methods include chemical structural modification, morphological transformations like templating, patterning, etc. Reactive centres are incorporated into the original polymer structure, which can act as linking points to chemically induct the sensing element to the polymer backbone. Reactive dithioacetal core was appended to fluorene containing conjugated polymer systems to detect mercury ions (*Ding et al., 2017*; *Shan et al., 2018*). Salicylaldehyde was substituted to poly phenyleneethynylene to detect iron(III) (*Thavornsin et al., 2018*). The imine group gets hydrolysed by iron(III) and enhance the fluorescence of the polymer. The broad utility of thiol-ene click chemistry in integration of sensing element was utilised by *Williams et al.* to modify an alkylene substituted fluorene for detection of pyrophosphates in seawater (*Williams et al., 2019*).

Application of Polymer Sensors

Conjugated polymer has become one of the foremost materials utilised in sensing industry. The vast variety of design criteria and structural features which can be added to the conjugated system allows detection of a wide range of analytes. This section illustrates the different types of analytes and their detection with sensing devices developed with conjugated polymers (*Fig. 2*).

Solid-State Analyte Sensor

Solid-state analytes include metal ions, pesticides, toxins, explosives, etc. Direct detection of those analytes is possible with Optical, mass, spectroscopy methods, energy-dispersive X-ray diffraction, and electrochemical methods. But most of the time the detection limit is quite high and in situ detection quite impossible. The conjugated polymers with enhanced optical properties and electronic properties could enhance the sensitivity and even reduce the detection limit. For metal ion analytes the conjugated polymer always contains some coordination sites along with hard-soft acid-base interaction make a good receptor for metal ions. Thiol incorporated conjugation polymer showing affinity towards mercury was fabricated into a Schottky diode (*Vintu and*

Unnikrishnan, 2018). The HOMO- LUMO values and bandgap of the polymer makes it suitable to work as a semiconductor. The interaction also yields a change in optical properties.

Detection of Nitroaromatic explosives is required in the field of forensic, military, airports, etc. Conducting polymer-based sensors are useful in their detection by forming a donor-acceptor complex with nitroaromatics. Electron rich conjugated polymer acts as a donor while nitro groups act as electron withdrawing group. Therefore, an electron-rich conducting polymer can form a donor-acceptor complex resulting in signalling response (Tanwar *et al.*, 2016).

Gas Sensors

As a result of industrial processes, transportation, combustion engines, etc a lot of toxic gases are emitted into the environment. NH_3 , H_2S , CO_2 , volatile organic compounds, hydrogen halide gas are some major gaseous pollutants. The severity and fatality of exposure to many of these gases makes it necessary for their real time detection and monitoring. Among the various receptors synthesised for gas sensing, conjugated polymers show enhanced electronic properties and hence useful for the detection of gases.

Diketopyrrolopyrrole (DPP)-based conjugated polymers have been widely utilised for gas sensing. An organic field effect transistor (OFET) sensor was fabricated with 2,5-difluorophenylene-dithiophene as electron donating active layer for highly sensitive detection of ammonia (NH_3) (Jeong *et al.*, 2017). Keto group of DPP acts as an electron acceptor and promotes interaction with Lewis basic NH_3 . High carrier mobility of DPP moiety imparts better sensitivity and enables reliable detection. The interaction is also observed to be reversible in nature facilitating reusability of the sensor. In a similar work, a DPP-fluorene based donor-acceptor copolymer was reported to have affinity to nitrogen dioxide (NO_2) over NH_3 (Li *et al.*, 2017). Redox behaviour and aggregation properties of the copolymer improved the selectivity and calibration of the OFET sensor.

Biosensors

A wide range of bioanalytics like proteins, virus, DNA, RNA, microRNA, nucleic acid related enzymes, sweat, glucose, cholesterol, etc. Immunology and clinical quantification assays require complex instrumentation and proficient technicians which generates a need for simple and reliable detection systems. CPs based protein detection is possible via conformational changes, fluorescence quenching and enhancement (Okada *et al.*, 2020). Glucose oxidase (GOx) enzyme-coupled organic electrochemical transistor for the detection of glucose was developed using a p-type and n-type polymers as cathode and anode which simultaneously functions as an enzymatic fuel (Ohayon *et al.*, 2020). The all polymer biofuel cell consists of copolymer of naphthalene dicarboximide (NDI) as acceptor and bithiophene (T2) as donor subunits with alkyl/glycol side chains randomly distributed on the backbone. The composition of glycol is much more compared to alkyl counterpart enhancing the interaction with aqueous medium. Glucose Oxidase enzyme is coupled with the glycol part of polymer. The polymer chain participates as the electron transfer reaction of glucose metabolism.

Strategies for Improving Selectivity

Polymer Nanocomposites

Nanoparticles and nanocomposite membranes have also been developed for metal ion sensing application due to their enhanced selectivity and sensitivity. Nanosizing exponentially increases the surface area to volume ratio. This amplifies the number of sensing sites thereby improving sensitivity (Fig. 3). In addition, selectivity can be effectively tailored by post synthesis surface modifications/treatments. Functionalized polyethersulfone & polypyrrole reduced graphene oxide (rGO) composite were also synthesised and reported for the detection of Cd^{2+} & Pb^{2+} , Cu^{2+} and Hg^{2+} which hinders the aggregation of polymer chains, enhancing the number of active sites for metal binding, thereby improving the sensitivity (Essousi *et al.*, 2019; Ghanbari, 2013; Hussein *et al.*, 2018; Suvina *et al.*, 2018). A ternary hybrid composite of polyaniline-alanine and rGO was also developed for real time analysis of Cd^{2+} , Pb^{2+} , and Cu^{2+} (Akhtar *et al.*, 2020).

Polymers Grafted on Substrate

Heterogeneous solid-state sensors are preferred over homogenous sensors due to their excellent reusability, stability and minimised contamination. A highly efficient luminescent microsphere sensor for copper ions was synthesised by the reaction of carboxylic acid terminated silica particles with luminescent lanthanide coordination polymers and is used for quenching effect of Cu^{2+} & Ni^{2+} (Cho *et al.*, 2014). Electro-polymerisation of aminopyrimidine groups with oxygen on graphene oxide results in the formation of GO anchored conjugated polymer which was reported to sense different heavy metal ions like Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} (Soliman *et al.*, 2016).

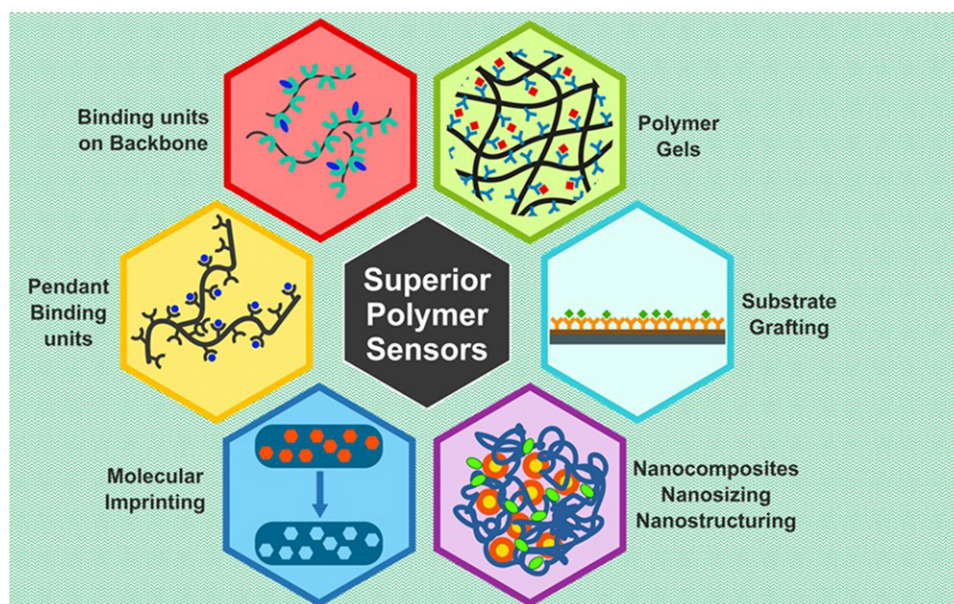


Fig. 3 Different Strategies for improving the selectivity of the polymer sensors.

Molecularly Imprinted Polymers

In molecularly imprinted polymers (MIPs), the compound of interest is used as template and functionalised monomers self-assemble around it. The subsequent removal of template leaves behind binding sites which are complementary to the shape of the template used. This ensures the high specificity and selectivity of the sensor. This technique has been extended to synthesise metal ion sensors with high affinity to a particular analyte. Metal ions are used as templates and the method is known as ion imprinting. A molecular imprinted electroluminescence was designed by using cobalt complex of bovine serum albumin (BSA) as template and used for detection of ions (Li *et al.*, 2019). Development of nanostructured ion imprinted polymer (IIP) for the detection of Pb^{2+} was also reported by copolymerisation of methacrylic acid- Pb^{2+} complex and ethylene glycol dimethacrylate. Pb^{2+} specific cavities were generated with carboxylic acid coordination site. Terthiophene polymer was used as a conducting layer beneath MIP to enhance the sensitivity and improve stability of glucose sensing (Kim *et al.*, 2017). The introduction of benzoic acid functionalised poly terthiophene layer generated additional response to the complexation of glucose on the MIP layer. Co-electropolymerisation of 3-acetic acid thiophene (AAT) and 3,4-ethylenedioxythiophene (EDOT) with 2,2'-methylenebis(2-methoxy-4-methylphenol) as template was reported for detection of condensed lignin marker (Gonzalez-Vogel *et al.*, 2019).

Conclusion and Future Prospects

In this book chapter, we discussed the recent developments in the field of conducting polymer-based sensors. The book chapter attempts to analyse the different structural features and synthetic methodologies adopted to improve the selectivity and specificity of polymer sensors. Polymers possessing coordinating centres on their backbone are found to be least selective. Polymer sensors bearing coordinating groups on side chain or as dendrimers seems to be an effective approach towards controlling the selectivity. A wide variety of previously known chelating ligands can be appended onto to the side chain. The density and size of the dendrimers play significant role in selectivity. Synthesis of polymer sensors into nanofiber, nanoparticles and nanocomposites improve their selectivity and sensitivity. Heterogeneous sensors prepared by grafting polymers onto various substrates also proved to be an effective method. It decreases the quantity of sensory material required for accurate sensing. Grafting also improved the selectivity in some cases. Molecular imprinting technique stands out among all other methods. The presence of template shaped cavities provides the highest selectivity and specificity among all other fabrication strategies. Imprinted polymers also possess much higher sensitivity than non-imprinted polymers. We have also discussed several advancements towards fabrication of polymeric sensing devices. However fast, accurate real-time on-site identification of polymer-based sensors still remains a challenge. Much efforts are required in developing cheap and durable sensors satisfying all the required criteria for practical applications.

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Metal-Organic Frameworks Based Chemical Sensors

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Abstract

Metal-organic frameworks provide unique features including high surface area, tailorable porosity, ease of functionalisation and post synthetic modifications and different host-guest interactions making them an ideal choice for chemical sensing. This chapter focusses on the MOFs based chemical sensors with understanding on different synthesis methods for MOFs. Various examples of MOF based chemical sensors based on electrochemical, optical, electronic, electromechanical and self-powered methods are summarised. These examples provide details on the readiness of MOFs for chemical sensors with high level of sensitivity and selectivity. The chapter also provides possible intriguing applications for MOF based sensors followed by conclusion and future perspective.

Key Points

- Metal-organic frameworks (MOFs) offers tailorable properties which are advantageous for chemical sensors.
- Considerations for MOFs selection as a sensing material.
- Synthesis methods of one-, two- and three-dimensional MOFs are summarised.
- MOFs based electronic, electrochemical, optical, electromechanical and self-powered chemical sensors are discussed in detail.
- Promising applications of MOFs based chemical sensors are summarised followed by future perspective.

Introduction

The advancement in micro/nanotechnology has significantly enriched the quality and reliability of sensors needed for various applications including health monitoring (Ji *et al.*, 2022; Bhattacharjee *et al.*, 2020) agriculture (Aliyana *et al.*, 2022), aquaculture (Manjakkal *et al.*, 2021a), environment monitoring (Chen *et al.*, 2022), robotics (Yogeswaran *et al.*, 2020; Neto *et al.*, 2022; Liu *et al.*, 2022a), rehabilitation (Liu *et al.*, 2022b; Ozioko and Dahiya, 2022), automation (Murali *et al.*, 2022), and space (Bonting, 1992; Li *et al.*, 2022) etc. Recent progress in flexible and printed electronics continue to advance these sensing solutions to enrich above areas and open new opportunities by allowing the detection of various chemical and biological analytes or parameters such as dopamine (Kafi *et al.*, 2020), glucose (Wang *et al.*, 2022a), tyrosine, (Dervin *et al.*, 2021) and creatinine (Luo *et al.*, 2021) for human healthcare (Dervin *et al.*, 2021; Jiang *et al.*, 2019). The rapidly ageing society and new forms of lethal diseases and rapidly changing environmental factors are also driving the research towards new types of chemical and biosensors sensors that are also portable and wearable (Ma *et al.*, 2022a; Zhu *et al.*, 2022; Zhao *et al.*, 2022) and as result numerous selective and sensitive chemical and biosensors have been reported in the literature (Karimi-Maleh *et al.*, 2021; Chen and Wang, 2020; Zhou *et al.*, 2021; Khandelwal *et al.*, 2019; Seol *et al.*, 2018; Schroeder *et al.*, 2019; Rahman *et al.*, 2011; Hosseini *et al.*, 2021; Khandelwal *et al.*, 2021a) using distinct working mechanisms, and exploiting the optical, piezoelectric, electrochemical, and enzymatic properties of various sensing materials (e.g., metal-organic frameworks (MOFs), 2D materials, conducting polymers, carbon nanotubes (CNT)) (Li *et al.*, 2015; Mross *et al.*, 2015; Bakker and Telting-Diaz, 2002; Skládal, 2016).

Among various materials for chemical sensors, the metal-organic frameworks (MOFs) are attractive and gained prominence in recent years. Discovered in 1990 s, MOFs are porous crystalline inorganic-organic hybrid materials. They comprise of metal ion (secondary building unit, SBU) linked to an organic ligand. The wide availability of metal-ions and organic linkers creates a possibility of infinite number of feasible MOF structures (Kalaj and Cohen, 2020; Zhou and Kitagawa, 2014; Furukawa *et al.*, 2013). The tremendous interest of scientific community in past two decades has led to the development of over 90,000 MOFs along with 500,000 predicted MOF structures (Moosavi *et al.*, 2020). Fig. 1 shows the timeline of important achievements in the MOFs based materials. The explosive growth in the MOFs is attributed to their functional and structural tunability. The porosity, chemical and thermal stability of MOFs can be tuned by the meticulous selection of the constituents. MOFs follow isorecticular principle i.e., MOFs of similar topologies can be produced from the different sizes organic ligands that have common symmetry or geometry. Although, the generated MOFs may have got enlarged pore volume or pore size (Furukawa *et al.*, 2013), they can easily undergo post-synthetic modification (PSM) adding an extra dimension for changing the pore reactivity.

MOFs have been used widely for the energy storage, energy harvesting, gas storage and separation, chemical sensors and catalysis (Furukawa *et al.*, 2013; Kuppler *et al.*, 2009). Chemical sensing is a process that uses a device comprising of sensing material that can undergo changes in the presence of a chemical substance or an analyte to be detected. Such changes then

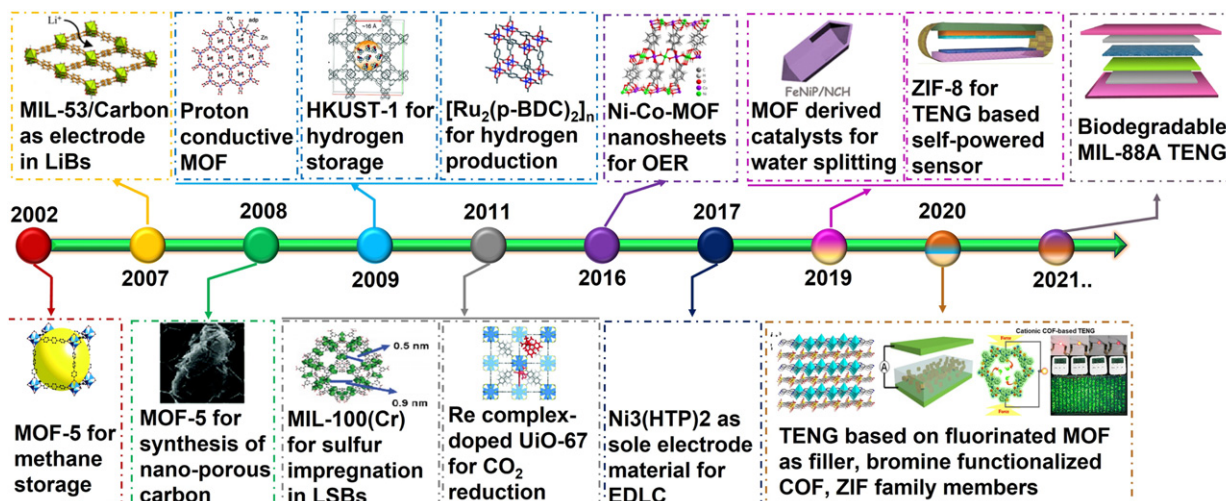


Fig. 1 Timeline of major achievements in MOF based materials for different applications. Reproduced with permission Khandelwal, G., Maria, N. P., Raj, J., Kim, S.-J., 2021a. Materials beyond conventional triboelectric series for fabrication and applications of triboelectric nanogenerators. *Advanced Energy Materials* 11 (33), 2101170. Copyright 2021, John Wiley and Sons.

transform into a measurable physical change by a transducer. The selective and sensitive detection of liquid chemicals, gases, volatile compounds and biomarkers are important for wide range of applications mentioned above (Manjakkal *et al.*, 2021a,b).

Majority of commercialised chemical sensors consist of inorganic-semiconductor or organic-polymeric films as the sensing material. These materials either adsorb or react with analyte molecules and the magnitude of detectable parameter could depend on the analyte concentration, analyte binding and physical properties. Despite of commercialisation, there is still a scope for improvement. One such case is H₂ sensor based on palladium, these sensors are susceptible to H₂S and CO poisoning. Similarly, the metal-oxide based chemical sensors typically work at high temperature. The exceptional properties of MOFs provide them with unique advantages as chemo-sensory materials over conventional materials (Shen *et al.*, 2022; Olorunyomi *et al.*, 2021, 2020). The properties responsible for extensive use of MOFs in chemical sensing include large surface area, tuneable porosity, chemical stability, ease of PSM, large library of central metal ions and organic ligands making them highly sensitive for chemical and biological analytes. Thus, MOFs can overcome many challenges like cross-sensitivity, selectivity that are also faced by other sensors.

This chapter focusses on the MOFs based chemical sensors. The chapter provides insights into various considerations for selections of MOFs and their synthesis methods for one-dimensional, two dimensional and three-dimensional structures. Later, MOF based chemical sensors involving different detection methods like electrochemical, chemicapacitive, chemiresistive, impedance, colorimetric, luminescence, electromechanical and self-powered etc. are discussed in detail. Finally, the application of MOFs based sensors are summarised followed by conclusion and future perspective.

Considerations for Selecting MOFs for Chemical Sensing

The performance parameters of chemical sensors include selectivity, sensitivity, limit of detection, response time, stability under sensing environment and reusability (Khandelwal and Dahiya, 2022). The porous crystalline MOFs can concentrate the analytes at higher levels and make them highly selective for the gas or vapour sensing (Furukawa *et al.*, 2013). Thus, MOFs do not require a sample preparation step involving concentrating the analyte using a porous material (Gu *et al.*, 2010). The sensitivity of a sensor to a large extent depends on the analyte binding or attachment on the sensing material and also on the analyte transport dynamics (Kreno *et al.*, 2012). The slow analyte transport eventually led to a slow response time. The selectivity of MOF towards analyte is possibly due to the size exclusion. The MOFs aperture and pore size are critical in the size exclusion. The molecules larger than the MOF aperture cannot be adsorbed making them selective to the molecules smaller than their aperture (Dincă and Long, 2005). The MOFs pore and aperture can be tuned by controlling the MOFs topology, linker size, linker shape, framework catenation etc.

The other possible mechanism of selectivity is the highly specific chemical interaction of the analyte with the MOF via formation of coordinate-covalent bond, hydrogen bonding or Mulliken type interactions. The MOFs can also be made selective to specific adsorbent or analyte by incorporating the desired functional groups during MOF synthesis. Further, MOFs can easily undergo PSM, allowing modification or addition of functional groups (Furukawa *et al.*, 2013; Kreno *et al.*, 2012). Lastly, certain analytes can preferentially interact with open metal sites of MOFs. One such example is reversible binding of NO to Cu (II), Co (II) or Ni (II) (Hinks *et al.*, 2010). The CO₂ molecules can interact with Co or Al based on the electrostatic interactions (quadrupole interactions) (Bourrelly *et al.*, 2005).

The sorption kinetics and thermodynamics play major role in the response time and regeneration of MOF based sensors. MOF based sensors can be regenerated by vacuum, washing or heating at high temperature as most of the guest or analyte molecules are

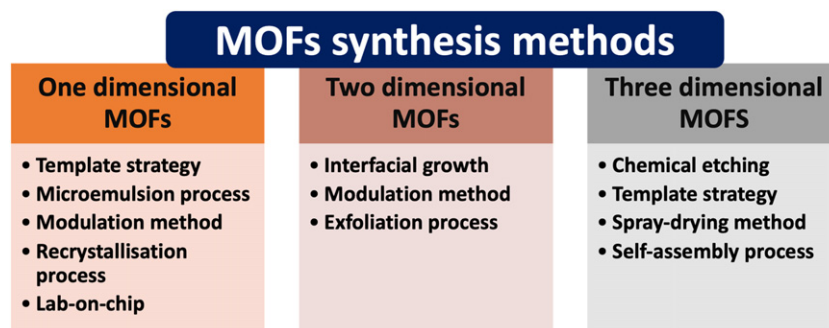


Fig. 2 Different methods for the synthesis of 1-D, 2-D and 3-D MOFs.

physisorbed on the MOFs. The response rate depends on the rate of guest or analyte diffusion which can be tuned with MOFs aperture size (Kreno *et al.*, 2012; Song *et al.*, 2010). MOF based chemical sensors are in early stage and sensing parameters can be further optimised in the near future.

MOFs Synthesis Methods

The MOF synthesis strategies allows control on the morphology and size in regard to their applications. This section describes the methods used to synthesise one dimensional (1-D), two dimensional (2-D) and three dimensional (3-D) methods (Fig. 2) (Xiao *et al.*, 2020).

One Dimensional MOFs

The 1-D MOFs structures include nanowires, nanofibers and nanorods which exhibits fascinating properties (Song *et al.*, 2016; Tsuruoka *et al.*, 2009). The preparation of 1-D MOFs is challenging compared to 0-D nanoparticles. Electrospinning is a straightforward approach to prepare nanofibers but the obtained fibres may not offer the same features as real MOFs as they also consist contain polymers, which can reduce the accessibility of the MOFs active sites. Some of the methods used to prepare 1-D MOFs are described below:

Template strategy

The 1-D MOFs can be formed in the polymeric pores or by using anodised aluminium oxide (AAO) as a template (Xiao *et al.*, 2020; Yao *et al.*, 2013). One such example is the preparation of ZIF-8 nanotubes using a polycarbonate membrane as a template (Arbulu *et al.*, 2018). In other work, 1-D MOF nanotubes were obtained by using MOF nanorods as the template (Li *et al.*, 2012). In template strategy, the template thickness, pore shape, pore size limits the MOFs length and diameter. In some cases, its challenging to remove the template and template removal may cause damage to MOFs structures. The template strategy method is high-cost and unsuitable for mass MOF production (Xiao *et al.*, 2020).

Microemulsion process

Microemulsion method allows controlled MOF synthesis in a specific direction. In this regard, $(\text{Gd}(\text{BDC})_{1.5}(\text{H}_2\text{O})_2)$, BDC = 1,4-benzenedicarboxylate) nanorods with an aspect ratio of 2.5–3 were prepared using water-in-oil microemulsion system. The ratio of water to oil or surfactant plays important role in controlling the size and morphology of nanorods (Rieter *et al.*, 2006). Microemulsion process can also be used for the preparation of 1-D lanthanides (Eu, Tb) based MOFs (Xiao *et al.*, 2020).

Modulation method

In this method, modulators are used to control the growth kinetics, allowing MOF growth in a specific direction leading to MOFs with different size and morphology (Zhan and Zeng, 2016; Umemura *et al.*, 2011). Salicylic acid was used as a modulator to control the growth process of Zn-MOF-74 nanorods (Pachfule *et al.*, 2016).

Recrystallisation process

Recrystallisation is a two-step process for the preparation of 1-D MOFs structures. In first step, an intermediate MOF structure is formed by the crystallisation of metal ions and ligands. Second step involves specific reaction conditions, leading to the transformation of MOF intermediate (Xiao *et al.*, 2020; Zou *et al.*, 2018). The transformation is accompanied by change in the crystal structure and morphology. The amorphous MOF particles were converted into 1-D MOF single crystal nanotubes (aspect ratio 400) by recrystallisation process (Zou *et al.*, 2018).

Lab-on-chip

Microfluidic approach can also allow the controlled synthesis of MOFs. A microfluidic platform with four input channels was used to prepare well aligned Cu(II)-Asp nanofibers with diameter in the range of 50–200 nm (Puigmartí-Luis *et al.*, 2011). Microfluidic approach is highly efficient and allows control on the reaction region to obtain 1-D MOFs.

Two Dimensional MOFs

The 2-D MOFs include nanosheets, thin films and membranes (Huang *et al.*, 2018; Zhao *et al.*, 2015). The 2-D MOFs are excellent choice for catalysis and sensing applications due to availability of abundant active sites. 2-D MOFs can be synthesised using bottom-up (interfacial and modulated synthesis) and top-down (mechanical and chemical exfoliation) approaches (Huang *et al.*, 2018; Zhao *et al.*, 2015; Zheng *et al.*, 2019; Li *et al.*, 2011).

Interfacial growth

As the name suggest, the growth process in this method occurs at the interface of two solvents containing ligand and metal ions (Xiao *et al.*, 2020). The CuBDC (BDC = 1, 4-benzenedicarboxylate) nanosheets with square lamellar morphology were obtained with an upper solution of copper nitrate and bottom BDC acid solution. The synthesis temperature can be used to tuned the thickness of CuBDC nanosheets (Rodenas *et al.*, 2015). Recently, liquid-phase epitaxy, combination of Langmuir-Blodgett (LB) and layer-by-layer (LBL) strategy were used to obtained MOF nanofilms on substrate and liquid surfaces (Sakaïda *et al.*, 2016; Otsubo *et al.*, 2012; Arslan *et al.*, 2011).

Modulation method

The use of surfactant during the growth process leads to formation of anisotropic MOFs. The 2-D Zn-TCPP (TCPP = tetra- (4-carboxyphenyl) porphine) nanosheets were obtained using polyvinyl pyrrolidone (PVP) as surface modulator (Zhao *et al.*, 2015; Wang *et al.*, 2016). In other work, gluconate salt was used as surface modulator to prepare Zn(bim)(OAc) nanosheets (Zhao *et al.*, 2018). The removal of surfactant is essential after the synthesis to allow access of MOF active sites. In certain cases, surfactant removal is a complex process leading to blockage of MOF active sites. Later, use of surfactant was omitted in heterogenous modulated hydrothermal synthesis method (Hu *et al.*, 2017).

Exfoliation process

The 2-D MOFs can also be prepared using solvent-induced delamination or ultrasonic exfoliation (Li *et al.*, 2011; Gallego *et al.*, 2013). The bulk MOFs can be transformed into MOF nanosheets by exfoliation process. The use of specific-solvent weakens the interlayer bond leading to few or monolayer MOF sheets. The Zn-MOF-2 bulk crystals were delaminated in acetone without any change in the crystal structure (Li *et al.*, 2011). Physical exfoliation in most of the cases destroys the MOFs in-plane structure. However, soft physical exfoliation methods (wet ball milling and ultrasonic peeling) can be used to obtain 2-D MOFs (Peng *et al.*, 2014).

Three dimensional MOFs

The hollow or porous 3-D MOF structures are advantageous for energy storage, catalysis and chemical sensing applications. Following are the methods for obtaining 3-D MOFs.

Chemical etching

Chemical etching is newly emerging method for obtaining 3-D MOFs. However, chemical etching can be used only to obtain few MOFs as it generally used acidic or basic etchant solution. Many MOFs are unstable in acid and base solutions (Xiao *et al.*, 2020). The 3-D ZIF-8 and ZIF-67 nanostructures were achieved by etching in xylene orange solution under controlled pH values (Avci *et al.*, 2015). In other work, acetic acid was used as etchant to obtain MIL-101 MOF single crystals from the bulk phase (Liu *et al.*, 2017).

Template strategy

Similar to 1-D MOFs, 3-D MOFs can also be prepared using soft or hard templates. The Fe-soc-MOF nanoparticles were formed in Pickering emulsion using colloidosomes as soft template (Pang *et al.*, 2013). In other work, HKUST-1 MOF was synthesised using vesicle template approach with cetyltrimethylammonium bromide (CTAB) as a modulator (Tan and Zeng, 2017).

Spray-drying method

Interfacial crystallisation process can lead to the formation of 3-D MOFs. In this regard, 14 different nanoMOFs were prepared by using spray-drying method. The hollow MOF architectures were formed by including volatile solvents into the microdroplets. The MOF precursor solution was crystallised at the liquid-gas interface (Carné-Sánchez *et al.*, 2013).

Self-assembly process

Self-assembly is ubiquitous ranging from the formation of sand-dunes to formation of colloids, monolayers and ribosomal proteins. A 3-D superstructure of Zn-MOF-74 nanorods was obtained by the self-assembly of 1-D MOF nanorods. The 1-D nanorods were obtained by hydrothermal transformation of Zn-MOF-74 nanoparticles. Moreover, modulators like CTAB, urea or PVP can be used to control the uniformity of Zn-MOF-74 superstructures (Zou *et al.*, 2019).

MOFs Based Sensors

The MOF based chemical sensors works on different transduction mechanism including electrochemical, optical, electro-mechanical, electronic and self-powered as explained in this section.

Electrochemical sensors

Electrochemical sensors translate the information linked with an electrochemical reaction (the reaction between the electrode and the analyte) in the form of a relevant signal. Since inception, they been used in a wide array of applications including environmental monitoring, medical diagnostics, food quality monitoring and detection of harmful chemicals (Kimmel *et al.*, 2012). This is due to their notable features such as easy miniaturisation, rapid analysis, excellent detection limit, low power requirements, outstanding repeatability and accuracy and low production cost. On the basis of signal acquisition, these sensors are majorly classified into three types: (a) potentiometric (measure voltage), (b) amperometric (measure current), and (c) conductometric (measure conductivity). Among these, amperometric method, which measures current as a consequence of an electroactive substance undergoing oxidation or reduction in the course of an electrochemical reaction, is extensively employed. The sensitivity and the selectivity are the key elements that necessitate consideration in optimising the performance and subsequent utilisation of the electrochemical sensor.

Metal-Organic Frameworks offer an attractive approach for electrochemical sensing due to porosity, ultra-high specific surface area and tuneable pore size and shape. The pores and the channels in MOF could load the target analytes with different sizes, shapes and polarity and could thus provide inherent shape and size selectivity for catalysis. The selectivity for guest analyte could be further enhanced by host-guest interactions occurring via hydrogen bonding, p-p interactions, open metal sites, Lewis acidic or basic sites in ligands and van der Waals interactions. Accessibility to a library of metal ions and organic linkers along with rational synthetic approaches provide immense possibilities for generating these combinations of the structural framework supports for catalysis. However, the poor conductivity and the inferior number of redox-active MOFs present huge roadblocks for the development of MOF-based electrochemical electrodes. Nonetheless, the porous nature of MOF allows a pathway for non-indigenous conductivity by infusing conducting materials such as metal nanoparticles, carbon-based structures and polymers with MOFs (Zhu and Xu, 2014). This facile combination is linked not only to noteworthy enhancements in the electrical conductivity but also to the improved mechanical strength of the composite. This subsection sheds light on representative examples of MOF-based electrochemical sensors for chemical and biosensing.

Nitrite sensors

There is an immensely growing demand for the development of nitrite sensors (NO_2^-) as it forms an essential component in drinking water and vegetables and has been extensively employed as a food preserving and fertilising agent (Singh *et al.*, 2021). An excess of nitride may lead to hypertension, stomach cancer and several other lethal diseases. Thus, routine monitoring with precise detection of nitride is critical. In this aspect, in one study a Cu-MOF/rGO hybrid was fabricated as a highly sensitive and selective electrochemical nitrite sensor (Fig. 3a) (Saraf *et al.*, 2016). Here, the porous nature of MOF furnishes a high surface area and the integration of rGO provides a synergistic effect to enhance the conductivity. The sensing activity was evaluated by modified glassy carbon electrodes (Cu-MOF/GCE and Cu-MOF/ rGO /GCE). It was observed that in the absence of nitrite ions, Cu-MOF/ rGO /GCE displayed very high currents, indicating its high charge transfer capability. Moreover, no oxidation peak was evidenced by bare electrodes, while in contrast both the modified electrodes (Cu-MOF/GCE and Cu-MOF/ rGO /GCE) exhibited a peak in the presence of nitrite ions thus representing the oxidation of nitrite into nitrate. However, Cu-MOF/ rGO /GCE exhibited a much higher current response than Cu-MOF/GCE pointing towards a higher potential for its employment for electrochemical activity. Immediately after the addition of nitrite ions, the amperometric response of the Cu-MOF/ rGO /GCE was rapid and was seen to achieve a steady state within 2 s, delineating a faster response. Furthermore, a linear response was demonstrated by the sensor in a wide range of 3–40 000 μM with a remarkable detection limit of 33 nm and a high sensitivity of $43.736 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$. Furthermore, the sensor was examined for its selectivity in the presence of common interfering ions like KCl, MgSO_4 , KNO_3 , NaAc, CaCl_2 and NaClO_4 . A distinguishable response following the addition of nitrite ions and no substantial response stemming from other ions affirmed its high selectivity towards nitrite detection.

Sweat sensors

Apart from the detection of inorganic analytes, the feasibility of MOF-based electrochemical sensors is also extended to biosensing due to their negligible cytotoxicity, high surface area and great thermal stability. As an example, a non-enzymatic electrochemical sweat sensor was demonstrated by using a copper isonicotinate $\text{Cu}(\text{INA})_2$ MOF (Fig. 3b) (Wang *et al.*, 2018). The authors in the study envisioned mimicking rime architecture as it possesses a high interior porosity altogether with a closely packed structure and is advantageous because of highly efficient absorption and transport characteristics. The MOF was grown on the surface of

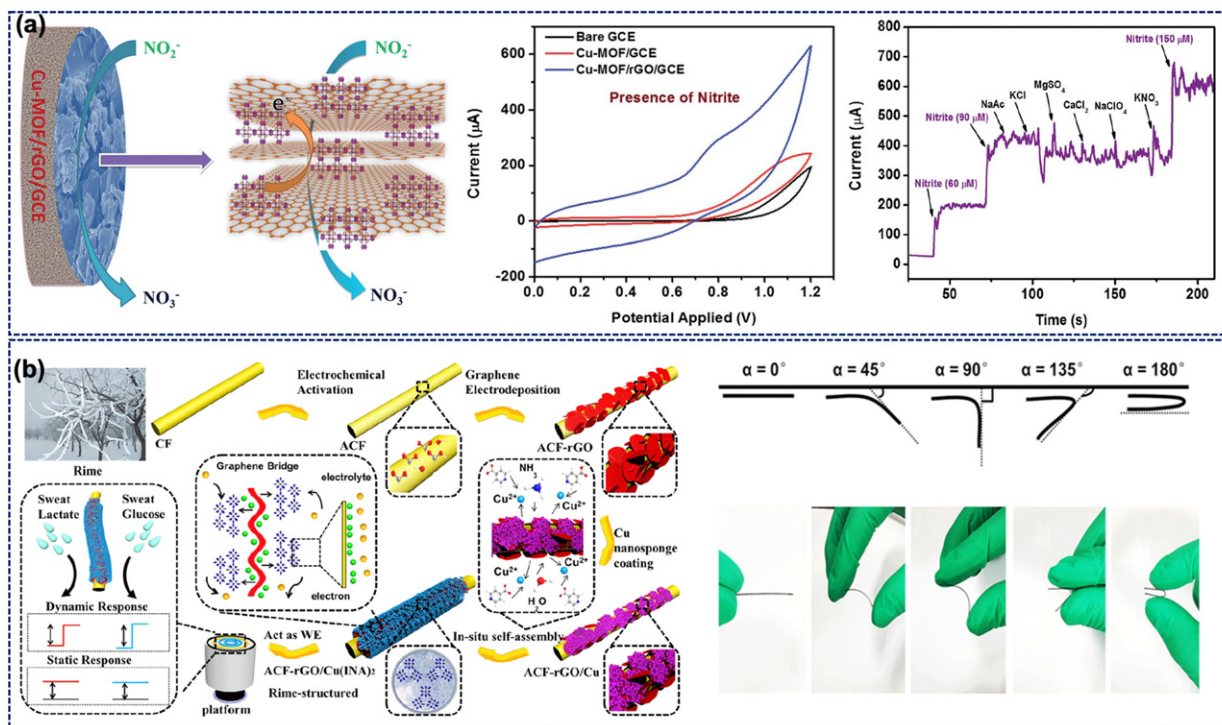


Fig. 3 (a) Schematic diagram depicting Cu-MOF/rGO/GCE nitrite sensor and its electrochemical activity towards nitrite sensing and selectivity test in presence of interfering ions. (b) Fabrication steps for the design of ACF-rGO/Cu(INA)₂ electrode and its optical images demonstrating flexibility. Reproduced with permission Saraf, M., Rajak, R., Mobin, S.M., 2016. A fascinating multitasking Cu-MOF/rGO hybrid for high performance supercapacitors and highly sensitive and selective electrochemical nitrite sensors. *Journal of Materials Chemistry A* 4 (42), 16432-16445. Copyright 2016, Royal Society of Chemistry. Reproduced with permission Wang, Z., *et al.*, 2018. Rimelike structure-inspired approach toward in situ-oriented self-assembly of hierarchical porous MOF films as a sweat biosensor. *ACS Applied Materials & Interfaces* 10 (33), 27936-27946. Copyright 2018, American Chemical Society.

graphene-coated activated carbon fibre (ACF-rGO) and was denoted as ACF-rGO/Cu(INA)₂. This technique offers fast diffusion of analytes and enhanced electron transfer kinetics. The composite was applied for electrochemical sensing of glucose and lactate simultaneously. The increase in the oxidation peak current in both cases indicates ACF-rGO/Cu(INA)₂ ability towards electrochemical detection towards glucose and lactate. A detection limit of 500 nM and sensitivity of $47 \mu\text{A cm}^{-2} \text{ mM}^{-1}$ was attained for the lactate while glucose detection delineated a detection limit of 50 nM and a sensitivity of $3139.7 \mu\text{A cm}^{-2} \text{ mM}^{-1}$. Moreover, the sensing ability was also evaluated in the acidic medium. The composite film was also subjected to mechanical stress to evaluate its flexibility and subsequent utility for wearable devices which was seen to demonstrate its sensing behaviour being independent of the bending states, thus ensuring its wide applicability.

Optical sensors

Optical sensors are based on light matter interactions (absorption, refraction, emission, reflection and transmittance. The presence of analyte leads to detectable changes in absorbance, luminescence, refractive indices and scattering (Shen *et al.*, 2022). Two most widely used optical sensors are colorimetric and luminescence-based sensors. The optical sensors based on other sensing mechanisms includes Bragg stacks, optical fibres, Fabry-Perot interferometers and diffraction gratings (Zhu *et al.*, 2021; Dalstein *et al.*, 2016; Zhu *et al.*, 2019; Hinterholzinger *et al.*, 2012).

Colorimetric sensors

Visual change in the colour of sensing material is the most straightforward sensing signal. Fig. 4 summarises five main MOFs chromogenic mechanisms viz., (a) change in the environment of centre metal ion in the MOFs, (b) guest-solvent exchange, (c) use of chromophoric ligands during MOF synthesis, and (d) extra-framework anion exchange and loading or encapsulating chromophores in the MOF (Feng *et al.*, 2021).

Change in the coordination environment of metal ions

Transition metal central ions like cobalt, copper, iron, cadmium and zirconium can change colour in response to various analyte or target molecules (Feng *et al.*, 2021). In such cases, target molecule alters the d-d transition of central metal ion leading to change in colour (Ullman *et al.*, 2018; Britt *et al.*, 2008; Cui *et al.*, 2014). One such example is volatile organic compounds (VOCs) responsive colour change

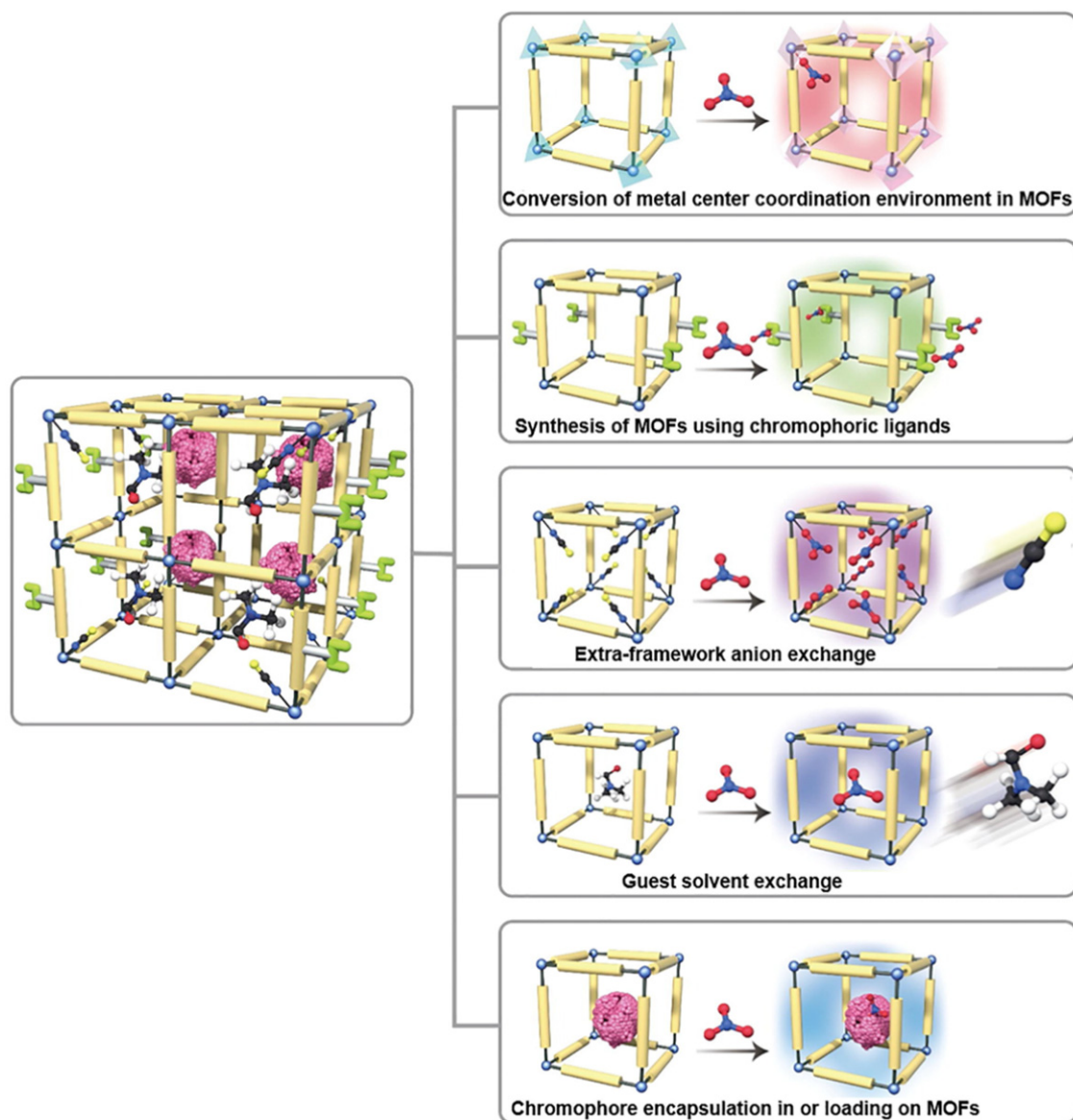


Fig. 4 Five different chromogenic mechanisms for MOFs. Reproduced with permission Feng, Y., Wang, Y., Ying, Y., 2021. Structural design of metal–organic frameworks with tunable colorimetric responses for visual sensing applications. *Coordination Chemistry Reviews* 446, 214102. Copyright 2021 Elsevier.

in the MOF comprised of Co^{2+} metal and 3-(4-pyridyl) benzoate (Dzesse *et al.*, 2018). The solvatochromism occurs in the presence of aprotic acetone, polar protic ethanol and methanol, Dimethylformamide (DMF), Dimethyl acetamide (DMA), Dimethyl sulfoxide (DMSO) and non-polar aprotic dioxane as shown in Fig. 5a. The change in colour is attributed to visible region changes in the d-d transitions (Dzesse *et al.*, 2018). In other work, alteration in the d-d transition led to colour change in the HKUST-1 MOF when exposed to H_2O (Ullman *et al.*, 2018). In other work, colour change for MOF FJU-56a in the visible region was observed in the presence of ammonia (NH_3). FJU-56a comprised of mixed valence (Co (II/III) metal ion coordinated to (tris-(4-tetrazolylphenyl) amine) ligand. The coordination of NH_3 to exposed nitrogen sites of ligand alters the coordination environment of Co ion and reducibility of NH_3 changes the valency of Co (II/III) leading to colour change from red to brown (Zhang *et al.*, 2018). Recently, $\{[\text{Cd}(\text{DPNDI})(2,6\text{-NDC})]\cdot 2\text{DMF}\}_n$ (DPNDI = N,N-Di(4-pyridyl) 1,4,5,8-naphthalenetetracarboxydiimide), a novel naphthalenediimide based MOF was reported for solvatochromic detection of electron rich organic amines. The solvatochromic behaviour was attributed to intermolecular electron transition from solvents to DPNDI ligand of MOF (Qin *et al.*, 2023). Fig. 5b shows the images of MOF in the presence of different amine solvents.

Guest – solvent exchange

Majority of as-prepared MOFs contains solvent like water, ethanol, methanol and DMF in their channels (Tang *et al.*, 2016; Li *et al.*, 2013; Kirandeep *et al.*, 2019; Yu *et al.*, 2014). These original solvents can be replaced by the external guest solvents and the process

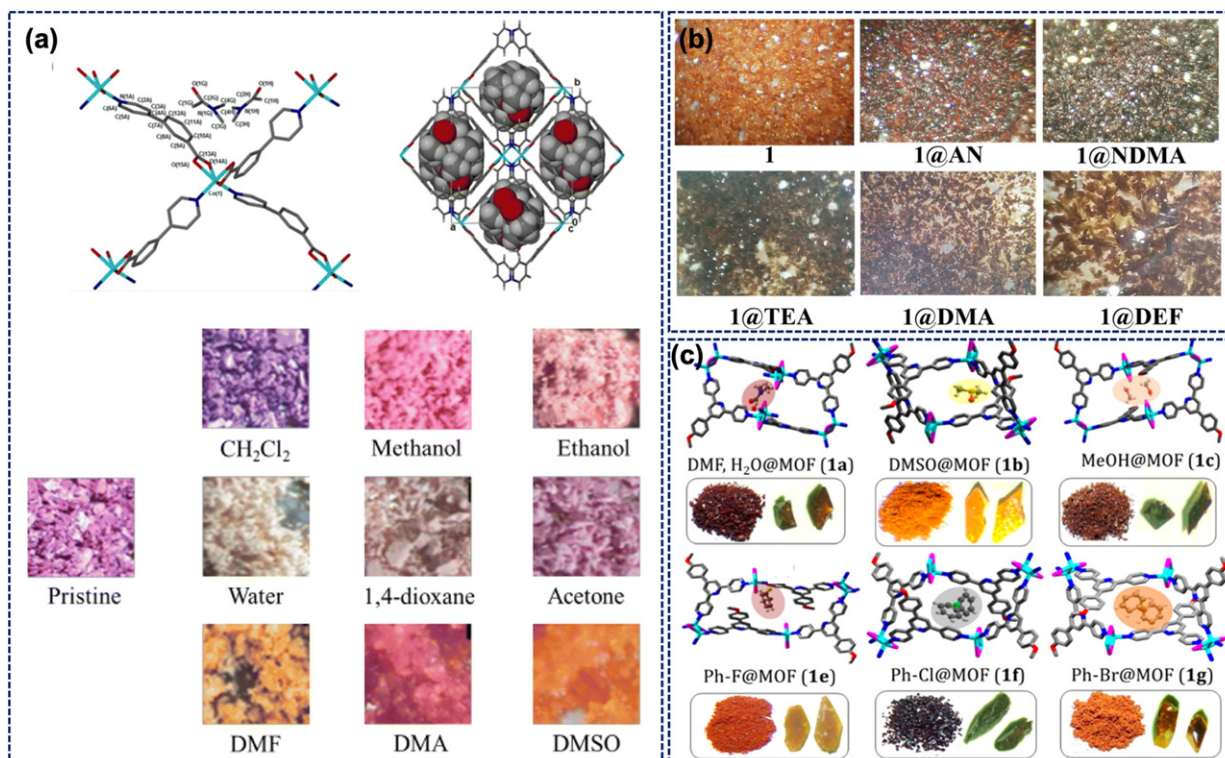


Fig. 5 (a) Solvatochromism of powder MOF after exposure to solvent. Copyright 2018, American Chemical Society. (b) Image of $\{[\text{Cd}(\text{DPNDI})(2,6\text{-NDC})]\cdot 2\text{DMF}\}_n$ upon exposure to different organic amine solvents. (c) Guest exchange exhibiting colour change under different polar solvent and monohalobenzene vapours. Adapted with permission Dzesse, C.N., Nfor, E.N., Bourne, S.A., 2018. Vapor sorption and solvatochromism in a metal–organic framework of an asymmetric pyridylcarboxylate. *Crystal Growth & Design* 18 (1), 416–423. Reproduced with permission Qin, L., *et al.*, 2023. A naphthalenediimide-based Cd-MOF as solvatochromic sensor to detect organic amines. *Journal of Solid State Chemistry* 317, 123660. Copyright 2022, Elsevier. Adapted with permission Khatua, S., *et al.*, 2015. Stable multiresponsive luminescent MOF for colorimetric detection of small molecules in selective and reversible manner. *Chemistry of Materials* 27 (15), 5349–5360. Copyright 2015, American Chemical Society.

is termed as guest-solvent exchange (GSE). The GSE leads to a colour change by altering the coordination geometry of metal leading to change in the d-d transition energy. In this regard, different aromatic VOCs (halobenzenes and nitroaromatic compounds), aliphatic VOCs (DMSO, MeOH) and heterocyclic VOCs (N-heterocycles) were detected using two-dimensional Cu(I)-MOF $[\text{Cu}(\text{L})(\text{I})]2n\cdot 2n\text{DMF}\cdot n\text{MeCN}$ ($\text{L} = 4'-(4\text{-methoxyphenyl})-4,2':6',4'\text{-terpyridine}$) (Khatua *et al.*, 2015). These guest solvents molecules replace the lattice solvents in MOF leading to unique colour change as shown in Fig. 5c.

Using chromophoric ligands during synthesis

The redox-active chromophoric ligands can be used during the MOF synthesis for colorimetric detection of analytes. The chromophoric ligands like tetrazine and bipyridinium derivatives shows colorimetric changes in response to reducible or oxidisable targets (Tan *et al.*, 2015; Nickerl *et al.*, 2015; Mallick *et al.*, 2015). In the presence of electron donors like NH₃ and amine, bipyridinium derivatives produce coloured free radicals as they receive electron from electron donors. Thus, such electron donors can be identified by the eye using MOFs composed of bipyridinium derivatives as ligand. One such example is Zn-based $[\text{Zn}_2(\text{L})(\text{PMC})_{1.5}] \cdot 12\text{H}_2\text{O}$ ($\text{H}_4\text{PMC} = \text{pyromellitic acid}$, $\text{L} = \text{a bipyridinium salt}$) MOF which changes its colour from yellow to dark blue in the presence of NH₃ vapour. Further, the used MOFs exhibited colorimetric reversibility through oxidation (Tan *et al.*, 2015). In other example viologen, a bipyridinium derivative was used as a ligand for the preparation of Cd (II) based MOF. The viologen can detect the different type of alkylamine vapour as shown in Fig. 6a. The viologen cations (V^{2+}) changes from $\text{V}^{\bullet+}$ radicals by accepting electrons from the alkylamine analytes (Sui *et al.*, 2018).

Extra-framework anion exchange

Cationic MOFs comprised of neutral ligand and metal ions can be used for the detection of different anions via extra-framework anion exchange due to positive charge in the framework. Thus, extra-framework anions can be coordinated to metal centre or settled in the void due to opposite charge (Feng *et al.*, 2021). These extra-framework anions can be exchanged with external anion resulting in colour change. One such example is cationic Cu (II)-MOF $[\text{CuL}_2(\text{H}_2\text{O})_{0.5}](\text{NO}_3)_2$, for colour responsive detection of different anions (Cl^- , I^- , SCN^- , Br^- and N^{3-}) as shown in Fig. 6b (Ma *et al.*, 2012). The MOF consist of extra-framework nitrate anions in channel that can be exchanged with the anions to be detected.

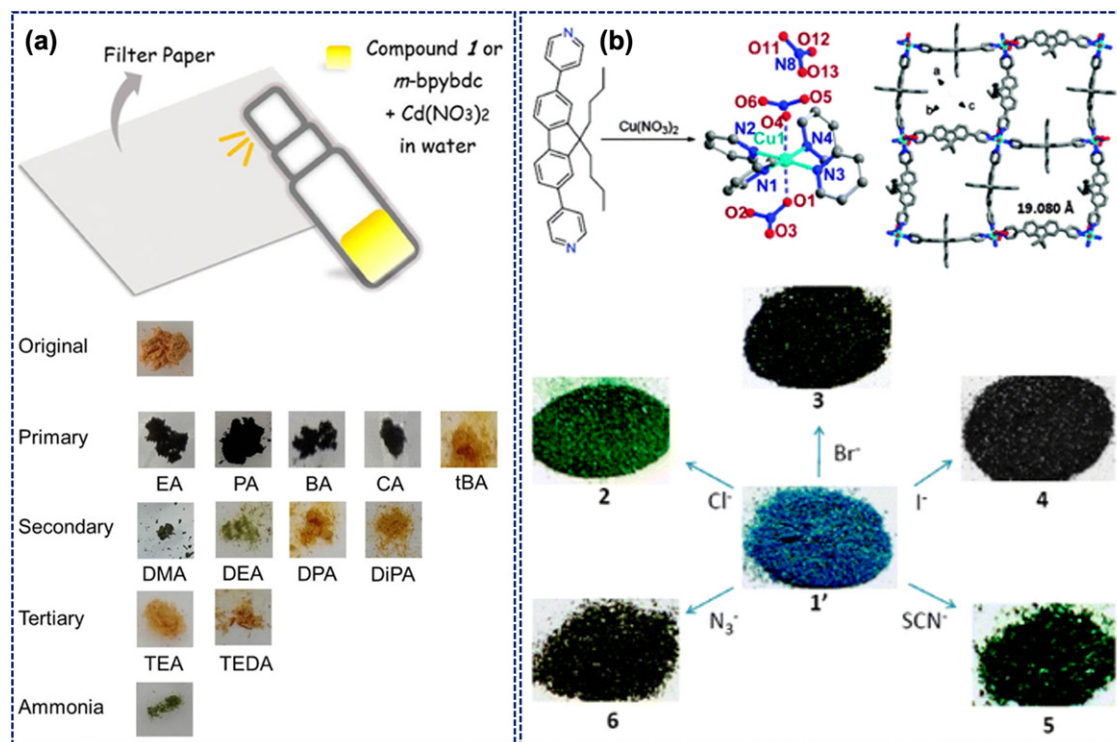


Fig. 6 (a) Photograph showing colour change in the presence of different amine vapours or solutions. (b) Cationic MOF ([CuL₂(H₂O)_{0.5}](NO₃)₂), showing colour change under exposure of different anions (Cl⁻, I⁻, SCN⁻, Br⁻ and N₃⁻). Reproduced with permission Sui, Q., *et al.*, 2018. Differentiable detection of volatile amines with a viologen-derived metal–organic material. *ACS Applied Materials & Interfaces* 10 (13), 11056–11062. Copyright 2018, American Chemical Society. Ma, J.-P., Yu, Y., Dong, Y.-B., 2012. Fluorene-based Cu(ii)-MOF: A visual colorimetric anion sensor and separator based on an anion-exchange approach. *Chemical Communications* 48 (24), 2946–2948. Copyright 2012, Royal Society of Chemistry.

Loading or encapsulating chromophores in MOF

The channels or voids of MOFs provide an excellent opportunity to encapsulate signal reporters like methyl viologen, cations, resorufin, coumarin and Nile blue to attain the colorimetric detection (Gong and Lu, 2013; Grünker *et al.*, 2012; Yoo *et al.*, 2019). Additionally, adsorption or covalent grafting methods can be used to load different chromophores like dithizone, rhodamine-based dyes, diethylthiocarbamate etc. onto MOFs (Radwan *et al.*, 2020; Zhang *et al.*, 2017; Shahat *et al.*, 2013; Khalil *et al.*, 2016). The chromophore loading or encapsulation has been reported for the colorimetric detection of Hg²⁺, picric acid, pyridine carboxylate, Cr₂O₇²⁻ etc (Yoo *et al.*, 2019; Radwan *et al.*, 2020; Zhang *et al.*, 2017; Li *et al.*, 2019).

Luminescence based sensors

Luminescence in MOFs often arises from four main sources (i) presence of photo responsive SBUs like lanthanide metals and d¹⁰ transition metal ions, (ii) extended π conjugation ligands in MOFs, (iii) charge transfer (CT) based luminescence which can be metal-to-metal CT, metal-to-ligand CT, ligand-to-ligand CT and ligand-to-metal CT and (iv) encapsulation of luminescent guests in the MOF pores (Shen *et al.*, 2022; Cui *et al.*, 2018; Wang *et al.*, 2022b; Gutiérrez *et al.*, 2022).

One excellent example of MOF based luminescent sensors is for the detection of nitro-containing explosives. Zn₂(bpdcc)₂bpee (bpdcc = 4,4'-biphenyldicarboxylate; bpee = 1,2-bipyridylethene), was demonstrated for the 1,4-dinitrotoluene (DNT) detection. In the presence of DNT, the MOF exhibited red shift in the emission (Lan *et al.*, 2009). The sensor showed better response time compared to conjugated polymer film-based sensors. Luminescent MOFs has been extensively used for the detection of VOCs. In this regard, Cu (I) based MOF [Cu₄L₄(Py₃P)₂]_n (Py₃P = tris(2-pyridyl)phosphine) was used for the detection of chlorinated VOCs (CH₂Cl₂, C₂H₄Cl₂ and CHCl₃) vapours (Liu *et al.*, 2020). In other work fluorescent dye (Nil red) was incorporated in ZIF-8 MOF to enhance the fluorescence. The prepared MOF was used for the detection of acetone, xylenes, methanol and toluene via fluorescent quenching (Olorunyomi *et al.*, 2020).

Electronic sensors

The technological advancements in the semiconductor industry have paved the way for the development of electronic sensors towards chemical sensing. These sensors transduce the changes in the electrical properties of MOFs i.e., impedance, capacitance, resistance and field effects upon its interaction with the target vapour. Although the poor conductivity of MOFs together with the difficulty of interfacing them into functional devices presents a major challenge, valuable research efforts have sprung up lately by

research groups which demonstrated porous MOFs with good electrical conductivity and understanding ways to tailor the electrical properties of existing insulating MOFs (Xie *et al.*, 2020). This section highlights four different MOF-based electronic device types and their configurations that have been utilised for chemical sensing.

Impedance sensors

Impedance spectroscopy measures the electrical impedance of the sensing material as a function of frequency of the applied current. This technique eludes the necessity to have bulk electrical conductivity, and thus materials with high resistance can be studied for sensing attributes.

It was in 2009 when the first MOF-based electronic sensor based on impedance spectroscopy was demonstrated (Achmann *et al.*, 2009). Five MOFs, namely, Al-BDC [Al(OH)(BDC)], Fe-BTC [Fe(III)(BTC)], Cu-BTC [Cu₃(BTC)₂], Li-doped Fe-BTC, and Fe (II)-doped Fe-BTC (BDC = 1,4-benzenedicarboxylate; BTC = 1,3,5-benzenetricarboxylate) were investigated for impedimetric sensing using the gases namely O₂, H₂, NO, CO₂, C₃H₈, ethanol and methanol. All the measurements were performed in the temperature range of 120–240°C and varying humidity conditions (0–2.5 vol%). Two types of device configurations were manifested. One by depositing the films of MOF onto interdigitated electrodes (IDEs) and the second by employing the pressed pellets. Among the studied MOFs, only Fe-BTC exhibited the change in the electrical response upon exposure to hydrophilic gases like ethanol, methanol and humidity with the latter displaying the highest sensitivity.

A detailed sensing mechanism was discussed later in 2013 on NH₂-MIL-125(Ti) (MIL: Materials Institute of Lavoisier) metal-organic framework by using complex impedance analysis (Zhang *et al.*, 2013). The sensor was fabricated by coating the MOF material on IDE electrodes. The MOF framework exhibits a great density of hydrophilic active sites such as titanium oxo-clusters and amino groups, wherein water molecules are easily adsorbed. Following the adsorption, a pathway for proton conduction is established which is responsible for a decrease in impedance values. When RH increased, impedance values decreased significantly from 11 % to 95 % RH, owing to the enhancement in the ion conduction due to adsorbed water molecules. The sensor demonstrated response and recovery times of 45 and 50 s, respectively.

Chemicapacitive sensors

A capacitor is an electrical component or a device that stores electrical energy by accumulating electric charges on opposite surfaces which are separated by an insulating layer and the capability to store these charges at a given potential refers to capacitance. By integrating MOF as a dielectric layer, alterations in the capacitance can be effectively produced upon the adsorption of the target vapour which underlines the basis of a chemicapacitive sensor.

These types of sensors are broadly categorized in two configurations namely: IDE and parallel plate geometries and become differentiated based on the geometry of these sensors. While in the case of IDE, the sensing layer is coated on the electrodes, the parallel plate mode requires the need to grow the MOF layer on the back electrodes followed by the placement of the upper electrode on top of the sensing material. The ease of fabrication of these sensors and their ready compatibility with the CMOS technology makes them highly promising towards chemical sensing.

A capacitor nanosensor was fabricated by employing Cu-BTC film directly grown on a copper substrate, acting as the back electrode, by electrochemical method (Hosseini *et al.*, 2016). The top electrode was fabricated using the connection spots of Ag paste on the top of the sensing film. The sensor was identified to show good linearity in the 1 MHz and therefore the sensing performance was evaluated at this frequency. Finally, the as-fabricated sensor was investigated for volatile inorganic compounds (VOCs) like methanol and ethanol. On an increase in the concentration of the target vapour, an increase in the capacitance value was evidenced. The change in the capacitance values was obtained to be higher in the case of methanol owing to its higher dielectric constant. The limit of detection was found to be 130.0 ppm for ethanol and 39.1 ppm for ethanol and methanol, respectively. Moreover, enhanced selectivity of the sensor over polar analytes was deduced by examining the sensor over nonpolar vapours like n-hexane.

In another study, the capacitive sensing layer was fabricated by in situ growth of fumarate-based fcu-MOF on an IDE-structured electrode for the detection of toxic H₂S gas (Yassine *et al.*, 2016). The sensor demonstrated remarkable sensitivity (100 ppb levels) and distinct selectivity towards H₂S over CH₄, NO₂, H₂, and C₇H₈.

Apart from the implementation of solely MOF as the sensing component, few studies also reveal deploying MOF-polymeric composites for gas sensing applications (Sachdeva *et al.*, 2017). In one study, nanoparticles of NH₂-MIL-53(Al) were embedded in a Matrimid polymer matrix with varying weight ratios (0 – 100 wt%) and drop-casted on capacitive devices. The capacitive response was increased by manifolds (almost 5 times) on the exposure of methanol and water on 40 wt% MOF-composite device than that compared to bare Matrimid coated devices indicating MOF NPs playing a major role in performance enhancement. Moreover, cross-sensitivity studies indicated the device's capability to kinetically differentiate between different alcohols with the disclosure of faster responsivity for methanol and water compared to ethanol and 2-propanol.

Chemiresistive sensors

Chemiresistive sensors exhibit a change in resistance in the active layer upon its interaction with the target analyte. These devices monitor response either via resistance measurement or conductivity analyses. Although the development of these sensors is one of the simplest, the dearth of MOFs with electrical conductivity hampered their effective utilisation as active chemiresistive sensing layer. The rapidly growing innovations in a range of synthetic approaches have enabled the discovery of MOFs with enhanced conductivity and have accelerated the development of chemiresistive sensors.

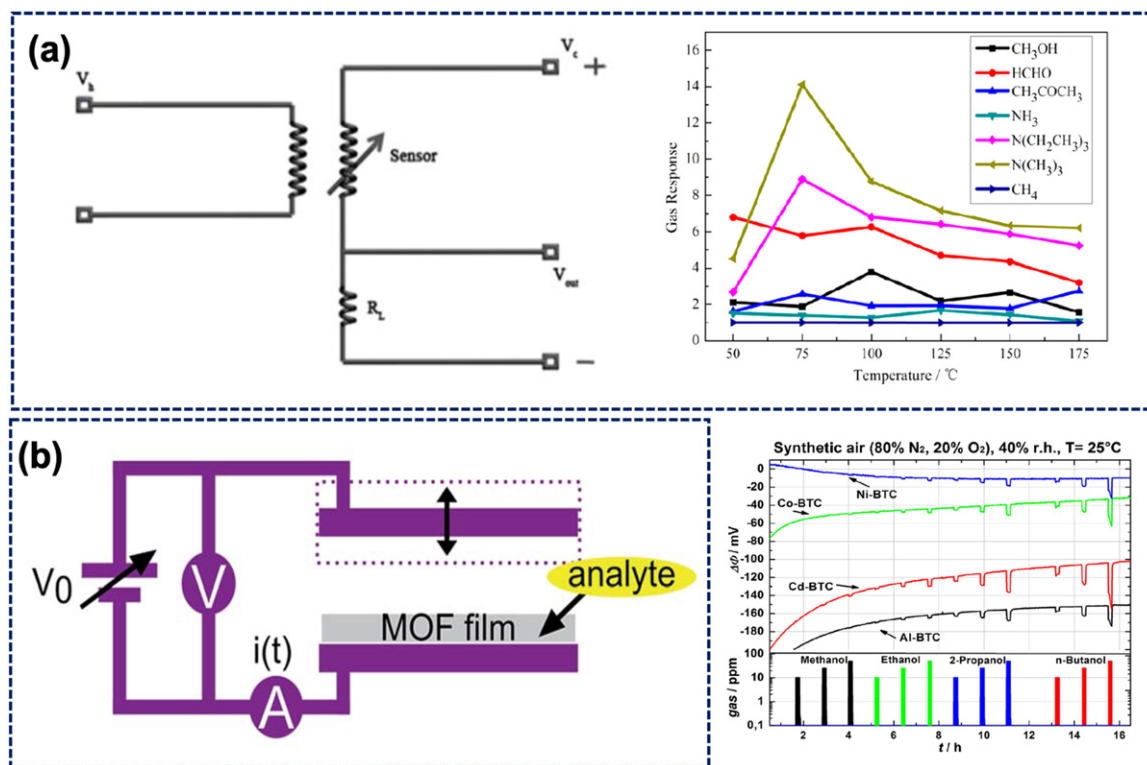


Fig. 7 (a) Scheme illustrating the operating principle of a resistive sensor and chemiresistive sensing of various gas demonstrated by $\text{Co}(\text{im})_2$ (im = imidazolate) MOF in the temperature range of 50–175 °C. (b) Schematic depiction of a Kelvin Probe Configuration. (c) BTC-linked MOFs as a work function-based sensor for the detection of alcohols at room temperature. Reproduced with permission Chen, E.-X., *et al.*, 2014a. Highly selective and sensitive trimethylamine gas sensor based on cobalt imidazolate framework material. *ACS Applied Materials & Interfaces* 6 (24), 22871–22875. Copyright 2014, American Chemical Society. Reproduced with permission Stassen, I., *et al.*, 2016. Towards metal–organic framework based field effect chemical sensors: UiO-66-NH₂ for nerve agent detection. *Chemical Science* 7 (9), 5827–5832. Copyright 2016, The Royal Society of Chemistry. Reproduced with permission Davydovskaya, P., *et al.*, 2014. Work function based sensing of alkanes and alcohols with benzene tricarboxylate linked metal organic frameworks. *Sensors and Actuators B: Chemical* 193, 911–917. Copyright 2013, Elsevier B.V. All rights reserved.

Zeolite imidazolate framework (ZIF) $\text{Co}(\text{mim})_2$ (where mim = 2-methylimidazolate), was employed as a formaldehyde gas sensor which could detect it at a concentration as low as 5 ppm (Fig. 7a) (Chen *et al.*, 2014b). However, the sensors required elevated temperature (150 °C) for their operation and suffered from slow response and recovery times. Subsequent studies by the same research group were conducted for trimethylamine (TMA) vapour sensing by deploying a similar kind of sensing layer $\text{Co}(\text{im})_2$ (im = imidazolate) (Fig. 1c) (Chen *et al.*, 2014a). The sensor exhibited a detection limit of 2 ppm for TMA at 75 °C. The response from the sensor was slow which could likely result from the low conductivity of the framework.

It was in 2015, when an electrically conductive 2D MOF $\text{Cu}_3(\text{HITP})_2$ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene), exhibiting a bulk conductivity of 0.2 S cm^{-1} was reported for chemiresistive sensing (Campbell *et al.*, 2015). This study reveals that targeting 2D frameworks based on a combination of redox-active metal centres with unique linkers containing p-conjugated structures such as the involvement of o-phenylenediamine linkages is a promising strategy for synthesising conductive MOFs. The device fabricated by drop-casting a dispersion of $\text{Cu}_3(\text{HITP})_2$ was able to detect sub-ppm levels of ammonia vapour under 60% relative humidity. Devices fabricated on an isostructural $\text{Ni}_3(\text{HITP})_2$ were also tested under identical conditions. No turn-on response exhibited by $\text{Ni}_3(\text{HITP})_2$ suggested the influence of synthetic variations impacting the functionality of the sensor.

Field effect transistor (FET) sensors

Endowed with the benefits of high integration, scalability, and tuneable electrical properties, FETs are emerging electronic devices which find applicability for a variety of technological uses (Yogeswaran *et al.*, 2020; Guo *et al.*, 2010; Paul *et al.*, 2022; Ma *et al.*, 2022b; Dahiya *et al.*, 2014). A FET is a device that employs an electric field to control/modulate the flow of current in a semiconductor. It consists of three terminals: source, gate and drain. Gate is separated from the source and drain by a dielectric layer. The response in the sensing parameters is monitored by variations in the gate-source voltage or drain-source currents. This concept has been widely used in ion sensitive field effect transistors (ISFETs) (Vilouras and Dahiya, 2021; Vilouras *et al.*, 2020; Shojaei Baghini *et al.*, 2022). Integration of MOF as the porous semiconducting material can bring about changes in the work function of the sensing MOF material upon exposure to analyte gas vapour which can be probed using the Kelvin probe method (Stassen *et al.*, 2016) as signal shift in the contact potential difference (CPD) response (Fig. 7b). The

Kelvin probe transducer consists of a modified stationary electrode connected to an oscillating reference electrode. The CPD emanates due to the Fermi level of electrodes and surface contribution linked with the adsorption of the gas vapour.

A floating gate FET gas sensor composed of Cu-1,3,5-benzenetricarboxylate MOF (Cu-BTC MOF) was presented towards sensing ppm levels of hexanal, pentanal, toluene, dimethyl ether, ammonia, hydrogen sulphide, ethanol and acetone (Pohle *et al.*, 2011). No change in work function was noticed in the case of hexanal and toluene while a strong response emanated from pentanal which rose with increasing temperatures. With not many differences in the chemical properties of these analytes, it was inferred that the pore size of MOF together with the size of analytes played a key role. On similar lines, the negligible response was ascertained from dimethyl ether in comparison with NH_3 and H_2S which responded very strongly due to size exclusion effects.

In an extended study, BTC-linked MOFs with varying metal sites (Co, Ni, Cd, Al) were examined as a work function-based gas sensing layer towards various linear alkanes and monohydric alcohols at room temperature (Fig. 7c) (Davydovskaya *et al.*, 2014). It was revealed that alcohol demonstrated stronger and concentration-dependent alterations in work function which was seen to rise with the length of the chain of alcohol groups whilst no detection was laid by alkanes with similar carbon chains. This selectivity was a result of the polarity of adsorption sites in MOF and the polar nature of gas molecules. Furthermore, the metal sites did not play any influential role in the sensing behaviour of the analytes.

Electromechanical sensors

MOF based electromechanical devices for chemical sensing includes quartz crystal microbalance (QCM), microcantilevers (MCL) and surface acoustic waves (SAW) (Olorunyomi *et al.*, 2021; Kreno *et al.*, 2012). Electromechanical devices are highly sensitive and MCL can even detect femtogram levels. For such devices, the high surface area and tunable porosity of MOFs are advantageous.

Quartz crystal microbalance (QCM)

QCM detects analytes by the change in the frequency of resonant vibration (Grate, 2000). QCM offers a very high sensitivity (~ 1 ng detection limit) compare to other mass-based detection methods. The quartz crystal sometimes coated with a layer to enhance the binding of the analyte. In MOF based QCMs, the centre gold electrode on a circular quartz crystal is coated or modified with the MOF. The Cu-BTC coated QCM was used for the detection of water vapours (Ameloot *et al.*, 2009). In other work, Cu-BTC grown on QCM was used to evaluate the MOF sorption properties (Biemmi *et al.*, 2008).

Microcantilevers (MCL)

MCL detects the analyte via dynamic mode or static deflection mode. In dynamic mode, the mass uptake leads to the cantilever oscillation frequency modifications. Static deflection works based on the strain-induced bending (Goeders *et al.*, 2008). A large tensile or compressive stress can be produced by small changes in unit cell. The removal of guest molecules from MIL-88 leads to a 23% change in the unit cell volume. CuBTC coated MCL was also demonstrated for stress-induced chemical detection (Kitagawa and Matsuda, 2007).

Surface acoustic wave (SAW) devices

In SAW devices, the analyte adsorption changes the frequency of the acoustic waves. The waves in 25–500 MHz were generated by a quartz oscillator (Kreno *et al.*, 2012). LBL grown MOF films on quartz were used for the frost point (-70 to 10°C) detection. In electro-mechanical devices, the sensitivity may be influenced the film morphology, thickness and the MOFs attachment (Kreno *et al.*, 2012).

Self-powered sensors

The expeditious development of miniaturised sensors leads to a new challenge of the continuous power source. The current governing power source are lithium-ion batteries which requires periodic replacement and composed of toxic ingredients. Furthermore, recycling a battery is challenging. The mechanical energy harvesters based on triboelectric and piezoelectric effect can be used as a sensor or as a power source to drive the sensors (Min *et al.*, 2021a,b; Deswal *et al.*, 2022, 2019). Out of the two MOF based triboelectric nanogenerators (TEGs) are demonstrated as self-powered chemical sensors (Khandelwal *et al.*, 2021a; Khandelwal and Dahiya, 2022). TENG works based on the conjoined effect of contact or triboelectrification and electrostatic induction. MOFs high surface area, porosity, flexibility in terms of size, functionality and ease of PSM making them ideal candidate for TENG based active chemical sensors. One such example is TENG comprised of ZIF-8 MOF as a positive and Kapton as a negative triboelectric layer (Fig. 8a) (Khandelwal *et al.*, 2019). The ZIF-8 was grown on ITO-coated PET for different cycles (15, 18, 20, 30 and 50-cyc). The 20-cyc MOF-TENG produced the highest output of 164 V and 7 μA in conventional vertical contact-separation mode. The as fabricated MOF-TENG was demonstrated for self-powered sensing of tetracycline (antibiotic) in the concentration range of 0–80 μM with a sensitivity of 3.12 $\text{V } \mu\text{M}^{-1}$. Fig. 8a also shows the decrease in voltage output with increase in tetracycline concentration. The sensor was selective and can be refreshed by a simple methanol washing process (Khandelwal *et al.*, 2019). In other work 1-D metal-biomolecule copper aspartate nanofibers (MBIOF) were used as an active layer for the fabrication of TENG in freestanding layer mode, vertical contact-separation mode and sliding mode. The contact-separation mode device (Fig. 8b) was demonstrated for thioacetamide (TAA) sensing. Fig. 8b also shows the voltage variation and device response with TAA concentration. The sensor exhibited a sensitivity of 0.76 V mM^{-1} with high selectivity (Khandelwal *et al.*, 2021b). MOFs based TENGs holds a promising approach for the development of self-sustaining self-powered chemical sensors.

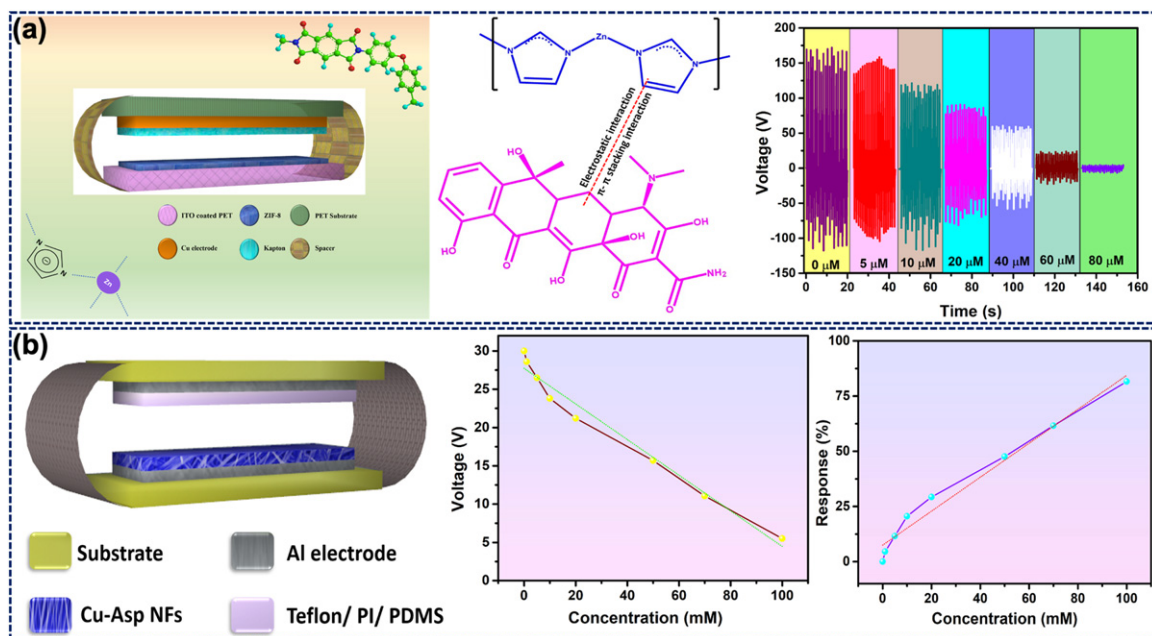


Fig. 8 (a) Design of ZIF-8 based TENG, sensing mechanism and voltage variation with tetracycline concentrations. (b) 3D illustration of Cu-Asp nanofiber based TENG, voltage and response of the device at different TAA concentrations. Reproduced with permission Khandelwal, G., *et al.*, 2019. Metal-organic framework: A novel material for triboelectric nanogenerator-based self-powered sensors and systems. *Advanced Energy Materials* 9 (14), 1803581. Copyright 2019, John Wiley and Sons. Khandelwal, G., *et al.*, 2021b. Metal-amino acid nanofibers based triboelectric nanogenerator for self-powered thioacetamide sensor. *ACS Applied Materials & Interfaces* 13 (16), 18887–18896. Copyright 2021, American Chemical Society.

Promising Applications of MOFs Based Sensors

MOF based chemical sensors are promising for food security, environmental monitoring, point-of-care (POC) devices, defence and robotics applications.

Environmental Monitoring

Large surface area and high porosity are distinctive features of MOFs. The MOFs can be used to detect the unfriendly chemicals in the environment. MOF based electronics and optical sensors are reported to detect environment contaminants like SO_2 , NH_3 , H_2S , NO, Nitrobenzene, VOCs, CO_2 and 5-Fluorouracil with high sensitivity (Kim *et al.*, 2019; Chocarro-Ruiz *et al.*, 2018; Chernikova *et al.*, 2018; Tao *et al.*, 2017; Smith and Mirica, 2017; Nazari *et al.*, 2016).

Food security

The wellbeing of livestock can be promoted by the detection of harmful chemicals in animal and plant products. MOFs are well documented to detect the toxic agrochemicals including phosphates, Kanamycin in milk and volatile plant oils (Yi *et al.*, 2021; Okur *et al.*, 2020; Luan *et al.*, 2017). MOF based sensors can revolutionise the sustainable agriculture and promote the quality of life.

Point-of-care (POC) devices

The integration of MOFs on biocompatible substrates was used to fabricate the POC MOF sensing devices. MOF based POC devices can be used to detect physiological conditions and biomarkers. Furthermore, MOF based sensing devices were coupled with smartphones and other mobile devices for digital health. One such example is the use of HKUST-1 MOF on face mask to detect sleep apnoea (Leelasree *et al.*, 2020). The MOF based POC devices were also used to detect the glucose, heavy metals, chlorpyrifos, Bisphenol A and antibiotics etc (Xu *et al.*, 2020; Li *et al.*, 2020; Al Lawati and Hassanzadeh, 2020; Zhang and Yan, 2019; Nagabooshanam *et al.*, 2019).

Defence

The chemical attacks involving use of triacetone triperoxide toxin, nerve agents and ammonium nitrate are threat to the mankind and global safety. The MOF based devices were demonstrated for chemical warfare decontamination and can find their spot for their detection in near future (Chen *et al.*, 2019; Mondloch *et al.*, 2015; Montoro *et al.*, 2011). The excellent performance of MOFs

in warfare decontamination can motivate the researchers to develop MOF based sensors to detect chemical warfares. Such MOF based sensors can be integrated on military wearables like gloves, helmets and wristbands etc.

Robotics

The MOF based devices can be used to develop robots which can sense multifunctional chemical features mimicking the humans. MOF based electronic nose can be used to detect the sense of smell while MOF based electronic tongue can be used for liquid detection. Further, MOF based e-skin can be used as chemical sensitive skins for robotic applications (Okur *et al.*, 2020, 2021; Wu *et al.*, 2020; Gustafson and Wilmer, 2018). The robots with such sensors can be deployed for remote monitoring to ensure the food and environment safety and for defence purposes.

Conclusion and Future Perspective

The field of MOF based sensors is continuously growing due to their advantages for numerous applications as mentioned in the chapter. The uniform MOF pore structure allows control on the mass transport and their electrochemical, electronic and optical properties, making them exemplary for the chemical sensing. The following challenges related to the development of MOF based chemical sensors can be focussed in the near future.

1. MOFs are not explored much for self-powered chemical sensors. The self-powered sensors are self-reliant as they do not need external power source. Self-powered sensors are much needed in applications such as wearable systems where portability is an important factor.
2. MOFs are brittle in nature. Mixing them with polymer or their palletisation reduces the accessibility of active sites. The 3D printing of pure MOF structures can help to extend the applications of MOFs for chemical sensing and allow device fabrication in different configurations.
3. MOF based colorimetric sensors are unstable due to MOFs instability in different pH conditions. MOF based colorimetric sensors are in early stage and need more attention as direct visualisation is most simple signal transduction.
4. Different MOFs can be integrated or incorporated in a single sensing device to enhance the selectivity or for detecting different analytes at the same time.

MOFs hold immense potential for chemical sensors based on different mechanism and addressing these challenges will further advance the field.

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Graphene-Based Touch Sensors

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Abstract

Graphene, a two-dimensional material with a honeycomb lattice and a thickness of a single carbon atom, is more robust than diamond but has a much lower density and is an excellent electrical conductor. These characteristics, along with the abundance of carbon in nature, have made graphene a fascinating research material with a wide range of applications. The objective of the article is to introduce the atomic structure of graphene, its basic material properties, and how the properties can be utilised to manufacture a large area of transparent touch sensors, as well as the challenges involved.

Key Points

- Graphene is a fascinating research material having exceptional opto-electronic and mechanical properties with a wide range of applications.
- The objective of the article is to introduce the atomic structure of graphene, its basic material properties, and popular synthesis techniques.
- The article also discuss how the unique properties of the graphene can be utilised to manufacture large area of transparent touch sensors.

Introduction

Last two decades have seen significant technological advances in communication (mobile phones, 4G/5G network, antennas), mobility (electric vehicles, batteries), robotics (flexible sensors, nano-generators) and many similar fields. The primary force behind these advances are the novel materials, and among which, graphene clearly stands out. Since the time it was first exfoliated from graphite by using the “scotch-tape” technique (Novoselov *et al.*, 2004b; Novoselov *et al.*, 2005), considerable efforts have been made to synthesise graphene using easier and cost-effective processes. Graphene has unique and excellent physical properties such as high thermal conductivity ($5000 \text{ W m}^{-1} \text{ K}^{-1}$) (Balandin *et al.*, 2008), high electron mobility ($250,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature and at an electron density of more than $2 \times 10^{11} \text{ cm}^{-2}$) (Bolotin *et al.*, 2008), high Young's modulus values (1.0 TPa) (Lee *et al.*, 2008), large surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) (Stoller *et al.*, 2008), high flexibility (Lee *et al.*, 2008) and better electrical conductivity (Cai *et al.*, 2009) and optical transmittance ($> 98\%$) (Bae *et al.*, 2010). Owing to these distinctive properties, graphene, and its derivatives have been used to develop various type of sensors (Dervin *et al.*, 2021; Khandelwal *et al.*, 2019b) and electronic devices (Yogeswaran *et al.*, 2018; Yogeswaran *et al.*, 2020) for diverse applications (Fig. 1), which range from human-machine interaction, robotics (Yogeswaran *et al.*, 2015; Kumaresan *et al.*, 2022b), wearable systems, displays (Nguyen *et al.*, 2012; Polat *et al.*, 2015), flexible electronics (Nguyen and Lee, 2021; Dahiya *et al.*, 2010), energy harvesting and storage (Pullanchiyodan *et al.*, 2020; Manjakkal *et al.*, 2019) and the health (You and Pak, 2013; Khandelwal *et al.*, 2019a; Bhattacharjee *et al.*, 2020a,b; Kafi *et al.*, 2020; Liu *et al.*, 2013) and environment monitoring (Presumido *et al.*, 2021), etc. (Beniwal *et al.*, 2023b; Paul *et al.*, 2022a; Liu *et al.*, 2022a; Chakraborty *et al.*, 2022; Forouzandeh *et al.*, 2022). Owing to exceptional opto-electronic characteristics, graphene also meets the requirements for a transparent conducting materials, which are in high demand in the touch based displays industry. This book chapter focusses on the fundamentals of graphene and how its unique properties could be utilised for the touch sensing applications.

The article is organised as follows: the atomic structure and various derivatives of graphene are discussed in section “Structure of Graphene”. Various properties of graphene are discussed in section “Properties of Graphene”. and this is followed by a brief history of research on graphene synthesis in section “Synthesis Techniques”. Various processes that are currently explored for synthesis of graphene are discussed in section “Synthesis Techniques” Touch Sensor applications. Finally, the use of graphene in touch sensing applications is presented in section “Touch Sensor applications” and followed by “Conclusion and Future Perspectives”.

Structure of Graphene

Graphene has a planar hexagonal or honeycomb structure, and all the atoms possess sp^2 hybridisation, as shown in Fig. 2 (Yang *et al.*, 2018). The short interatomic distance (a_0 is 0.142 nm) in graphene provides it with remarkable mechanical strength, reflected by its high Young's modulus (around 1 TPa) and tensile strength (130 GPa) (Geim and Novoselov, 2007a). In honeycomb structure, an out-of-plane π bond is made up by $2p_z$ orbitals of the C-atoms which are perpendicular to the planar

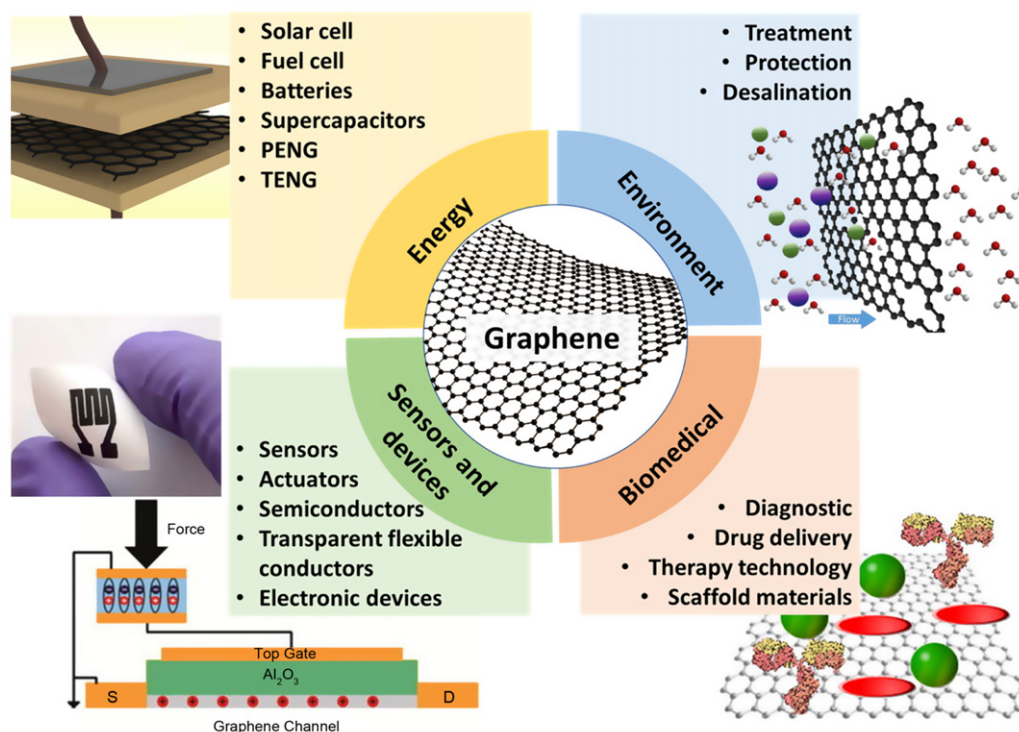


Fig. 1 Summary of few applications of graphene and its derivatives. Reproduced from Bokhari, S.W., Siddique, A.H., Sherrell, P.C., *et al.*, 2020. Advances in graphene-based supercapacitor electrodes. *Energy Reports* 6, 2768–2784. Reproduced under the terms of creative common license (CC-BY 4.0), Copyright (2020) Elsevier. Beniwal, A., Ganguly, P., Aliyana, A.K., Khandelwal, G., Dahiya, R., 2023a. Screen-printed graphene-carbon ink based disposable humidity sensor with wireless communication. *Sensors and Actuators B: Chemical* 374. Reproduced under the terms of creative common license (CC-BY 4.0), Copyright (2023) Elsevier. Yogeswaran, N., Navaraj, W.T., Gupta, S., *et al.*, 2018. Piezoelectric graphene field effect transistor pressure sensors for tactile sensing. *Applied Physics Letters* 113. Reproduced under the terms of creative common license (CC-BY 4.0), Copyright (2018) American Institute of Physics. Liu, J., Cui, L., Losic, D., 2013. Graphene and graphene oxide as new nanocarriers for drug delivery applications. *Acta Biomaterialia* 9, 9243–9257. Presumido, P.H., Primo, A., Vilar, V.J.P., Garcia, H., 2021. Large area continuous multilayer graphene membrane for water desalination. *Chemical Engineering Journal* 413.

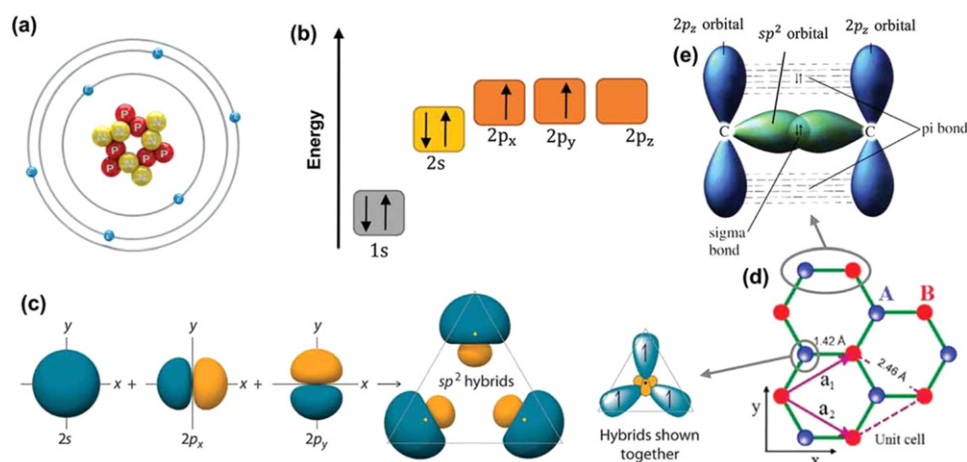


Fig. 2 (a) Atomic structure of carbon. (b) Electron configuration in C atoms. (c) The sp^2 hybridisation of C to form graphene. (d) In the crystal lattice of graphene, where A and B are C atoms belonging to different sub-lattices, a_1 and a_2 are unit-cell vectors. (e) σ and π bond formed by sp^2 hybridisation. Adapted from Yang, G., Li, L., Lee, W.B., Ng, M.C., 2018. Structure of graphene and its disorders: A review. *Science and Technology of Advanced Materials* 19, 613–648. Reproduced under the terms of creative common license (CC-BY 4.0), Copyright (2018), Taylor and Francis.

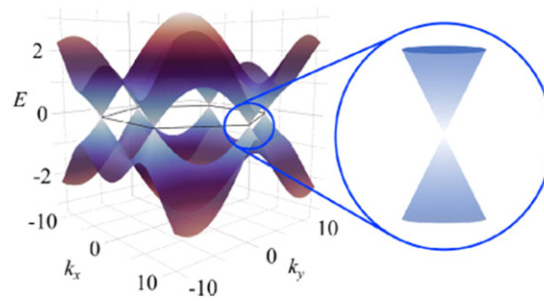


Fig. 3 Electronic band gap structure of graphene. Reproduced with permission (Kotakoski, 2021) Atomic and electronic structure of graphene. Graphene.

structure, while an in-plane σ bond is formed by the sp^2 ($2s$, $2p_x$ and $2p_y$) hybridised orbitals. The weaker out-of-plane π bond lead to weaker van der Waals force, and hence the adhesion between adjacent graphene layers is relatively weak (Schäffel, 2013). The distance between the planes or layers in graphene is 0.34 nm. When the numbers of layers exceed 10, the multi-layered graphene is known as graphite as its electronic and electrical properties resemble that of graphite.

Band Structure

The band structure of graphene, as estimated from tight binding density functional theory (DFT) calculations, can be seen in Fig. 2 (Wallace, 1947; Reich *et al.*, 2002). In this band structure, the Fermi level corresponds to $E = 0$ and the valence and conduction bands meet at six points known as Dirac points, at $E = 0$. So, the positive energy values correspond to the conduction band, while the negative ones correspond to valence bands. Because of no energy gap between the valence and conduction bands, single-layer graphene (as well as double-layer graphene) are zero band gap semiconductors. However, with an increasing number of layers, there is an overlap of valence and conduction bands, and thus the behaviour of higher-layer graphene structures becomes metallic (Razaq *et al.*, 2022). For this reason, derivatives of graphene are used as electrodes in applications such as energy devices and various sensors. The band gap in graphene can also be tuned by the addition of defects or functional groups in graphene. For further details related to the band structure of graphene, the reader may refer to literature (Yang *et al.*, 2018; Dreyer *et al.*, 2010; Reich *et al.*, 2002).

The unusual and complicated band structure of single-layer graphene gives rise to unique and exotic electronic transport properties. The charge carriers in graphene, known as fermions, (in the case of graphene, the charge carriers are described using Dirac's equation rather than Schrodinger's equation), are massless. The reported electron mobility values in graphene is more than $25,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Bolotin *et al.*, 2008). This also makes it attractive for molecular electronics, for example, graphene-based interconnects and field-effect transistors (Liu *et al.*, 2019) (Fig. 3).

Graphene Derivatives

The honeycomb structure of graphene is also regarded as the starting point for other members of graphene family such as carbon nanotubes (CNTs), graphene nanoribbons (GNRs), fullerenes etc. In fact, the folding or moulding of graphene can lead to above allotropes. For example, graphene sheets can be folded to form 0D bucky-balls or C_{60} fullerenes, 1D CNTs, 2D graphene nanoribbons or 3D graphite structures (Geim and Novoselov, 2007a). Because of the narrow band gap (approximately 1.6–1.9 eV) (Pan *et al.*, 2020), unique electronic properties and distinct structure, fullerenes find applications in the field of photovoltaics and photocatalysis (Fu *et al.*, 2008; Mroz *et al.*, 2007). On the other hand, CNTs and GNRs have wide variety of applications because of their distinct mechanical, electronic, and structural properties. CNTs generally have a diameter between 1–100 nm and could be single-walled (SWCNT) or multi-walled (MWCNT) (Zang *et al.*, 2015). The Young's modulus and tensile strength for both SWCNT and MWCNT are lower in comparison with graphene. However, the band gap in MWCNT is nearly 0, while in SWCNT, it lies in the range of 0–2 eV (it depends on its configuration, i.e., zigzag, armchair or chiral) and in both, the charge carrier mobility is similar to that of graphene. Thus, they are extensively used in nanocomposites for drug delivery (Bianco *et al.*, 2005), pressure sensing (Shakthivel *et al.*, 2019), gas sensing (Septiani and Yuliarto, 2016), energy storage (Manjakkal *et al.*, 2021), hydrogen storage (Lee and Lee, 2000), and other applications. GNRs are produced when 2D graphene sheets are confined within one direction, i.e., one of its dimensions is relatively larger than the other dimension, and thus, it behaves like a quasi-1D material. Since pure graphene lacks a band gap, it is not an ideal material for logic device applications (Shen *et al.*, 2015). However, in GNRs, because of quantum confinement effects, there is an onset of band gap which introduces the semiconductor behaviour. The band gap in GNRs is dependent on their width as well as atomic edge structures. The charge mobility in sub 5 nm GNRs is around $\sim 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and it increases with the width of the GNR (Li *et al.*, 2008). These make them suitable for electronics and optoelectronics applications.

Besides the above forms, the chemical and functionalised form of graphene such as GO and reduced graphene oxide (r-GO) are also explored for application in energy, biomedical, sensor, supercapacitor, water-purification and analytical sciences fields (Bobnar *et al.*, 2018; Dervin *et al.*, 2021; Dimiev and Eigler, 2016; Joshi *et al.*, 2021; Razaq *et al.*, 2022; Soni *et al.*, 2020; Wilson *et al.*, 2009). GO comprises of incorporation of oxygen atoms into a carbon scaffold. The presence of both sp^2 and sp^3 hybridise atoms in GO, allows tuning of surface and electronic properties of pristine graphene. For example, while graphene is insolvable in

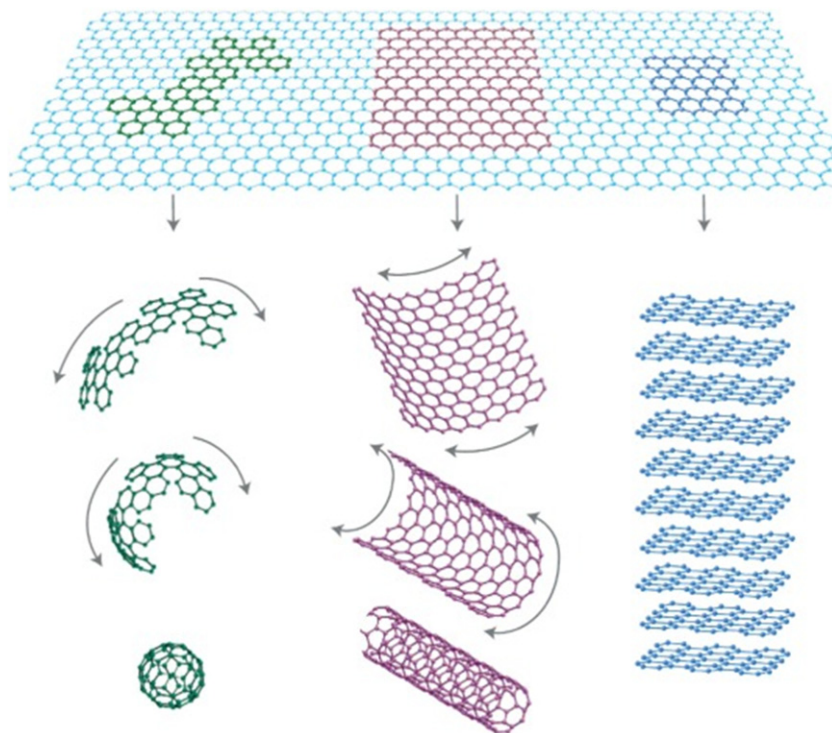


Fig. 4 Carbon allotropes from graphene: zero-dimensional (0D) buckyball, one-dimensional (1D) CNT, and three-dimensional graphite (3D). Reproduced with permission Saxena, T., Loong Peng Tan, M., Arora, V.K. 2022. Introduction to graphene. Graphene, Nanotubes and Quantum Dots-Based Nanotechnology.

water, GO can be dissolved (Georgakilas *et al.*, 2016). The synthesis of GO is generally easier and economic and typically involves the chemical oxidation of graphite using oxidising agents such as H_2SO_4 , HNO_3 , KClO_3 etc., followed by dispersion and exfoliation in water or other organic solvents (Dimiev and Eigler, 2016; Georgakilas *et al.*, 2016). When GO is reduced using strong reducing agents like hydrazines, oxygen atoms are removed from GO, thus producing r-GO. The properties of GO are quite far from the properties of pristine graphene sheets. However, when GO is transformed into r-GO, some of the graphene properties are restored in r-GO. For example, GO is electrically insulating in nature, while r-GO is conductive (however, its conductivity is lower than that of pristine graphene). GO can be further functionalised facilitating surface modification of GO. This surface modification of GO offers various advantages owing to its remarkable optical, electrical, electrochemical, and biocompatibility properties (Pierleoni *et al.*, 2018; Razaq *et al.*, 2022; Yang *et al.*, 2009). The research on graphene and its various applications has also led to research on other promising classes of 2D materials such as silicenes, transition metal dichalcogenides, boron nitride etc., (Geim and Novoselov, 2007a; Sarkar *et al.*, 2014; Oughaddou *et al.*, 2015; Georgakilas *et al.*, 2016). Thus, graphene has also acted as the catalyst for many other classes of nanomaterials and their composites. (Fig. 4).

Properties of Graphene

Graphene is more robust than diamond but has a much lower density and is an excellent electrical conductor. Such features, along with the abundance of carbon in nature, make graphene a fascinating material with a wide range of applications. As mentioned earlier, graphene possesses high degree of optical transparency, high carrier mobility, and thermal conductivity, in addition to mechanical flexibility, robustness, and environmental stability. This section looks into the various optoelectronic and mechanical properties of graphene.

Carbon has six electrons ($[\text{He}] 1s^2 2s^2 2p^2$); among them, 4 of the outermost electrons are available for chemical bonding during the excited state, as $2s^1 2p^3$. In the case of graphene, each carbon atom shares one electron with nearby carbon and forms three sigma bonds, leaving one of the outermost electrons available for conduction. The free electrons are available above and below the graphene sheets, forming π -bonds that enhance the carbon bonding and the bonding-antibonding of the π -orbitals define the electronic properties (Fig. 5 (a)). Graphene has an excellent carrier mobility of $> 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and even a "minimum" conductivity of $4e^2/h$ even when the carrier concentration tends to be zero (Geim and Novoselov, 2007a). Numerous experiments have also confirmed graphene's extremely high carrier mobility. For example, it has been observed that on an h-BN substrate graphene has carrier mobility as high as $0.8 \times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Dean *et al.*, 2010). Electrons travelling through the bi-directional graphene have a linear relationship between energy and momentum, massless Dirac fermions (Bonaccorso *et al.*, 2010).

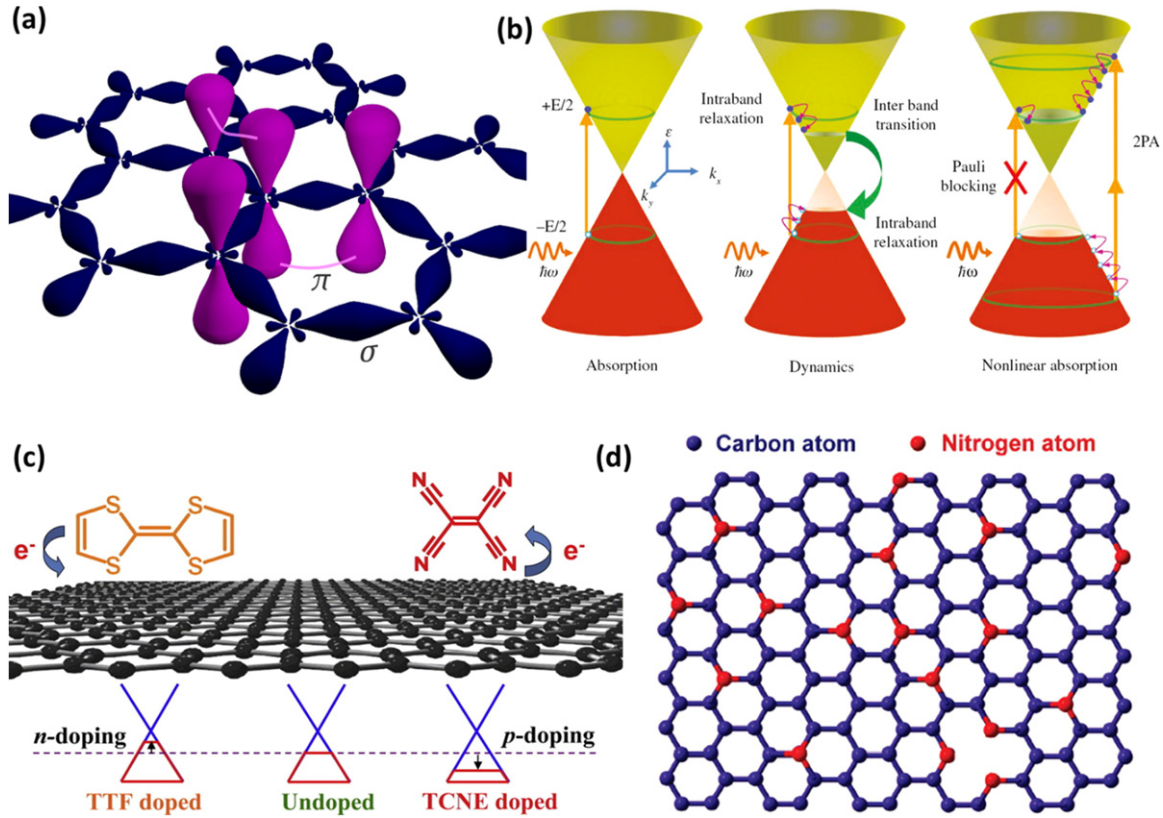


Fig. 5 (a) The π -bond structure of 2D graphene that defines its electronic properties. (b) Schematic representation of linear and non-linear absorption of graphene. (c) Surface charge doping in graphene. (d) Illustration of graphene doping by heteroatom substitution. Reproduced from You, J.W., Bongu, S.R., Bao, Q., Panou, N.C., 2018. Nonlinear optical properties and applications of 2D materials: theoretical and experimental aspects. *Nanophotonics* 8, 63–97. Reproduced under the terms of creative common license (CC-BY 4.0), Copyright 2018. Choudhury, D., Das, B., Sarma, D.D., Rao, C.N.R., 2010. XPS evidence for molecular charge-transfer doping of graphene. *Chemical Physics Letters* 497, 66–69. Wei, D., Liu, Y., Wang, Y., *et al.*, 2009. Synthesis of N-doped graphene by chemical vapor deposition and its electrical properties. *Nano Letters* 9, 1752–1758. Copyright (2009) American Chemical Society.

Transparency is one of the requirements for placing current touch sensors on top of screens, and graphene is quite popular as a transparent conducting material that has huge potential in touch-sensing applications. The transparency is highly contradictory for a material like graphene due to its good electronic properties. When the graphene surface is exposed to light, the electrons get excited and move from the valence to the conduction band by absorbing the photonic energy. Theoretically, because of the zero-band gap nature, graphene can absorb any optical radiation irrespective of the wavelength and have flat absorption characteristics from 300 to 2500 nm (Bonaccorso *et al.*, 2010). The photoconductivity of the single-layer graphene depends on the fine-structure constant (α): (Wang *et al.*, 2019).

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \quad (1)$$

Where c is the speed of light, e is the elementary charge, $\hbar$ is the reduced plank constant, ϵ_0 is the permittivity, and the linear transparency (T) of the single layer graphene is given as:

$$T = \frac{1}{(1 + 0.5\alpha\pi)^2} \approx 1 - \pi\alpha \approx 97.7\% \quad (2)$$

A typical monolayer of graphene absorbs 2.3% in the visible range spectrum and is expected to increase linearly with the number of layers, as $n\pi\alpha$, with each layer absorbing an additional 2.3% of light. This is promising for touch sensing applications as the sheet resistance can be highly improved using multi-layer graphene without sacrificing much of the optical transparency. It also makes it possible to characterise the number of graphene layers using optical absorption. In reality, multi-layer graphene is an excellent absorbent of light. Indeed, a single or few-layer graphene can satisfy the transparency requirements due to its low thickness, which is good enough to meet electronic needs due to its excellent carrier mobility.

Graphene also exhibits non-linear optical transparency which increases with light intensity (Vermeulen, 2022). The energy band at the Dirac point is filled at the low light exposure intensity, and as a result graphene maintains a steady absorption rate. As the carriers are stimulated from the ground state to higher states more quickly than they are relaxed, the energy close to the Dirac point gets filled at sufficiently high light intensities. This increases the optical transmission, and the absorption no longer

remains linear, as shown in Fig. 5 (b) (Wang *et al.*, 2019). The non-linear saturable absorption of graphene is given as:

$$\alpha(N) = \frac{\alpha_s}{1 + N/N_{sat}} + \alpha_0 \quad (3)$$

Where α_s is the saturated absorption coefficient, α_0 is the unsaturated absorption coefficient, N is the optically induced charge carriers, and N_{sat} is the saturated concentration of the carriers (Obraztsova *et al.*, 2021).

The optoelectronic properties of graphene can be improved by doping (Choudhury *et al.*, 2010). Controlled doping can be used to fine-tune the fermi level of graphene, especially when creating high-quality electrical contacts and carrier injection with other materials. The doping mechanisms can be either by surface charge transfer or substitutional (Hu *et al.*, 2022). In surface charge doping, the electronically interacting dopants are introduced by either physical or chemical adsorption to the surface, which can either donate or extract electrons. In contrast, the substitutional doping introduces dopants into the graphene lattice in case of that can alter the electronic structure. Even though doping may improve the performance, it is still important to emphasise that the structural integrity and uniformity are important for superior device performance. The structural integrity of the graphene can be preserved with the adsorption of dopant while the doping is highly unstable and non-uniform. In the case of substitutional doping, heteroatoms have been introduced and incorporated into the lattice during the CVD growth of the graphene. Strong covalent bond formation between the heteroatom and graphene ensures high stability. At the same time, they can introduce lattice disorders and defects that can act as scattering centres of carriers and reduce the carrier mobility (Lee *et al.*, 2018).

In surface charge doping, the dopants are anchored into the graphene surface by interfacial forces without forming any chemical bonds. The nature of doping, i.e., *n*-type or *p*-type, is decided using the position of the fermi level and the highest occupied molecular orbital (HOMO) - lowest occupied molecular orbital (LUMO) levels of graphene and the adsorbate, respectively. If the LUMO energy of the adsorbate is below the graphene fermi level, electrons will flow from the graphene to the adsorbate, creating *p*-type doping. Similarly, the electrons will flow from the adsorbate to the graphene if its HOMO energy is higher than its fermi level, which will eventually introduce *n*-type doping in graphene. The doping level is decided by the amount of adsorbate and depends on the exposed graphene area. Reversible adsorption and desorption are the challenges to doping stability. Some of the reported adsorbates include P_2O_5 (Park *et al.*, 2015), 1,5-naphthalenediamine (Dong *et al.*, 2009), as *n*-type and PMMA (Koo and Ju, 2015), NO_2 (Schedin *et al.*, 2007), as *p*-type dopants.

Graphene consists of sp^2 hybridised carbon atoms that are densely packed in 2D with a honeycomb structure. The heteroatoms, which can act as either electron donors or acceptors, can be deliberately introduced into this matrix to alter the electronic structure in substitutional doping. Halogens (F, Cl, Br, and I) can extract electrons from graphene, by forming covalent bonds with sp^3 hybridisation, which results in *p*-type doping. Like conventional doping, by substituting the neighbouring elements of carbon in the periodic table, such as B and N, both *p* and *n*-type doping can be induced. Since the 2D honeycomb structure of graphene is highly stable, very high energy is required to disturb the lattice structure and to replace carbon from the matrix. Substitutional doping of N and B can be achieved at the high-temperature CVD growth stage of graphene by introducing either individual sources of carbon and heteroatoms or a single precursor containing both the carbon and heteroatoms by preserving the thermodynamic stability.

There is an ever-growing demand for lightweight and flexible electronic materials, especially for shape-confirmable applications in wearable systems, robotic e-skin, and portable energy harvesters (Liu *et al.*, 2022b; Shakthivel *et al.*, 2021; Nikbakhtnasrabadi *et al.*, 2021; Dahiya *et al.*, 2020). Recently graphene was deposited on top of an electroplated Cu circuit present on a polyimide substrate through low-temperature CVD technology (Lu *et al.*, 2021). A bending test of a 2.5 mm radius, performed for over 100,000 cycles, showed that the sample covered with graphene is more durable, while the uncovered sample broke down after 60,000 cycles. In addition, the graphene coating could also prevent Cu oxidation for extended periods of time. Graphene can also be coated on solar cells to develop self-powered touch sensors (Dahiya *et al.*, 2019b; García Núñez *et al.*, 2019; Núñez *et al.*, 2017b). Such works confirm the excellent flexible properties, mechanical durability, and corrosion resistance properties of graphene.

Nowadays, touch screens are an inevitable component in any human-machine interface; they need a high-quality large-area material with good electrical conductivity and transparency so that they can be installed over displays and other modern devices where additional mechanical flexibility and conformability are needed. Indium tin oxide (ITO) is currently the forerunner for touch screens due to its excellent optoelectronic properties. However, due to its ceramic nature, ITO is highly brittle with low strain strength, it is vulnerable to micro-cracks and very expensive due to the scarcity of indium. Polymers, such as PEDOT:PSS, and metallic nanostructures (Nair *et al.*, 2020a; Nair *et al.*, 2021a; Sharma *et al.*, 2022) have been recently reported as substitutes but their use is limited due to poor stability and surface properties. The above-mentioned properties, including high optical transparency ($> 97\%$), carrier mobility ($> 10^5 \text{ cm}^2/\text{Vs}$), excellent mechanical strength, flexibility and conformability, low weight, and low cost, define graphene as an ideal candidate for the development of transparent touch sensor and will be extensively discussed in section "Conclusion and Future Perspectives".

Synthesis Techniques

History of Graphene Synthesis

Graphite, containing the many layers of 2D graphene sheets, was initially used as precursor to synthesis graphene. As the adhesion between different layers in graphite is high, so the initial attempts to synthesis 2D graphene used the idea of inserting certain chemicals/molecules between the layers in graphite leading to formation of compounds known as graphene intercalation compounds (GICs). In 1841, Schafhaeutil (1840b,a) was the first person to synthesis GIC using potassium followed by exfoliation with sulphuric

and nitric acids. Several other intercalants and exfoliants have been used since that time, including other alkali metals, fluorides, transition metals (iron, nickel, and many others), and other organic compounds (Inagaki, 1989; Hérold *et al.*, 1996; Liu *et al.*, 2002; Dreyer *et al.*, 2010). However, in 1859, a British scientist Brodie came up with a modified method using stronger oxidants such as KClO_3 and acids like sulphuric and nitric acid, intercalation of layers of graphite as well as oxidation of its surface happened leading to formation of another form of graphene i.e., graphene oxide (GO) (Brodie (1859,1860)). Nearly after a century, Boehm and co-workers produced lamellar single layer structures known as reduced-GO by chemical reduction of dispersions of GO in dilute alkaline media with hydrazine, hydrogen sulphide, or iron(II) salts at elevated temperature (Boehm *et al.*, 1962). This thermal reduction process is still used widely to carry out chemical exfoliation of GO and similar products. Later, in 1968, Morgan and Somorjai (1968) studied the adsorption of several gaseous molecules like CO, C_2H_2 etc., on Pt(100) surface at high temperatures. A year later in 1969, the data from this experiment was analysed by May and he found out that multiple layers of a material having graphite like structure were found on the Pt surface (May, 1969). Soon after, Blakely and co-workers used similar approach and studied the adsorption of organic gases of different metallic surfaces like Ni(100), Ni(111), Pd(100) etc., and found single- and multi-layered carbon compounds on the surfaces of these metals (Blakely *et al.*, 1970; Eizenberg and Blakely, 1979; Hamilton and Blakely, 1978; Hamilton and Blakely, 1980; Patil and Blakely, 1974). In 1975, using a totally different approach Van Bommel *et al.* (1975) produced monolayer graphite structure by sublimation of Si from SiC(0001) at elevated temperatures and ultrahigh vacuum. The structures of these monolayer graphite were consistent with the structure of graphene. In 1997, IUPAC formalised the definition of graphene as "The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed" (Mcnaught and Wilkinson, 1997). However, later researchers started using mechanical exfoliation technique to produce single or multi layered graphene structures. To this extent, in 1999, Ruoff and co-workers attempted a mechanical exfoliation of highly ordered pyrolytic graphite (HOPG) pillars and they produced lamellae structures containing few layers of grapheme (Lu *et al.*, 1999; Xuekun *et al.*, 1999). However, it was not before 2004 when Geim and co-workers presented a reliable and robust process by which single layered (0.8 nm) thick monolayer carbon layer or graphene was formed by repeatedly peeling HOPG using the famous "scotch tape" method (Geim and Novoselov, 2007a; Novoselov *et al.*, 2004b,a). This work led to series of other works and scientists were able to investigate the structure and properties of graphene as well as graphene was started being used for various applications.

Modern Synthesis Techniques

A wide variety of techniques have been employed for the fabrication of graphene, as highlighted in section "History of Graphene Synthesis"/"Touch Sensor Applications" (Fig. 6). The structural morphology, quality, and properties of the graphene highly depend on the synthesis method; hence, it is critical. In general, the synthesis of 2D materials can be classified as top-down and bottom-up approaches.

Top-down approaches

Top-down approaches convert bulk materials into nanosheets by overcoming Van der Waal's force between the individual nanosheets. Top-down approaches include mechanical, liquid phase, and electrochemical exfoliations, graphene oxide reduction and arc-discharge methods.

Mechanical exfoliation is a conventional technique of producing a single/finite layer of graphene from its multi-layer counterparts, such as graphite, using interfacial peeling by controlling the exfoliation kinetics such as force, speed, etc. (Whitener and Sheehan, 2014). The most famous technique for isolating graphene sheets includes the scotch tape method, where the mechanical cleavage of the thinner layer from a graphite crystal using an adhesive tape was proposed by Novoselov *et al.* (2004b). The thin flakes obtained by the scotch tape method can be further thinned to multi-layer and even single-layer by repeated micro-mechanical cleavage using the tape. Although the approach is simple and does not require sophisticated equipment, it is time-consuming, and the original graphite crystal size constrains the area.

The liquid-phase exfoliation approach offers the advantages of being more processable, less expensive, having a quicker preparation period, and being able to prepare in larger quantities (Yi and Shen, 2015). The van der Waal's force between the graphene sheets must be overcome to produce a single layer from multi-graphene-layered graphite (Elumalai *et al.*, 2020). The dispersant-solvent solution enters the graphene sheet layer and interacts with its surface to create stable liquid phase dispersion using various exfoliation processes, such as ultrasonic, mechanical, and electrochemical, to overcome the van der Waals attraction between layers. In ultrasonic exfoliation, the graphite dispersed in solvents such as N-methyl pyrrolidone (NMP), and cyclopentanone, will be treated with ultrasonication, and due to the intense shear force experienced between the layers, the graphene sheets will be separated (Hernandez *et al.*, 2008). Even though ultrasonication offers low cost and ease of operation advantages, long-term ultrasonication can induce defects and is also not scalable due to various parameter dependencies, including sonication power, time, frequency, solvent concentration and so on (Río *et al.*, 2017). In mechanical, various shearing and ball-milling techniques were employed to produce high-quality graphene (Bonaccorso *et al.*, 2016). Electrochemical exfoliation is one of the popular techniques to produce graphene from graphite due to its advantages of fast, high efficiency, and environmental protection (Parvez *et al.*, 2014). In this method, an applied voltage drives ionic species in an electrolyte to intercalate into the graphene electrode, thereby increasing the interlayer distance and, finally, will exfoliate graphene layers. The major disadvantage of the technique is that it requires a continuous electrically conducting monolith of graphite. There is a high chance that the graphite monolith disintegrates and becomes discontinuous due to the expansion during the electrochemical exfoliation, and the process stops (Achee *et al.*, 2018).

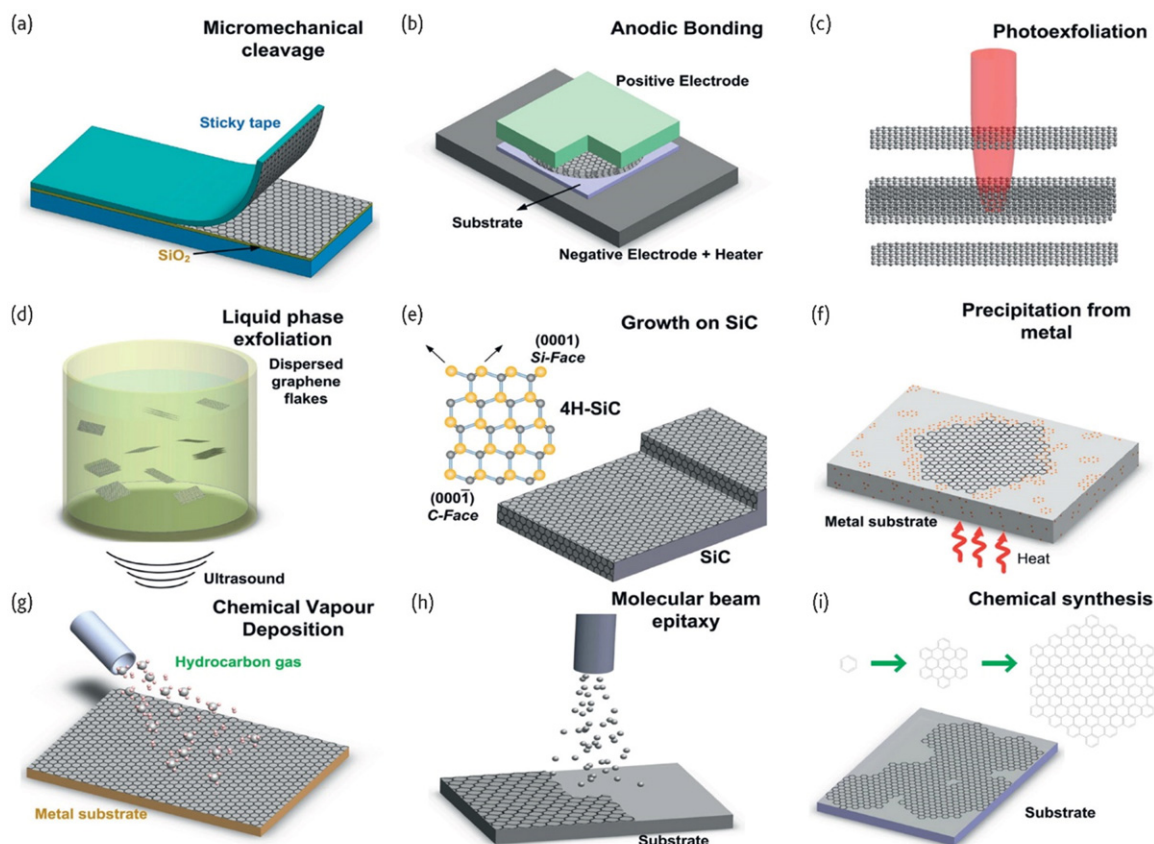


Fig. 6 Schematic of the popular graphene production techniques. (a) Micromechanical cleavage (b) Anodic bonding. (c) Photo-exfoliation (d) Liquid phase exfoliation (e) Growth on SiC (f) Segregation/precipitation from the carbon-containing metal substrate (g) Chemical vapour deposition (h) Molecular Beam epitaxy (i) Chemical synthesis using benzene as the building block. Adapted from Bonaccorso, F., Lombardo, A., Hasan, T., *et al.*, 2012. Production and processing of graphene and 2d crystals. *Materials Today* 15, 564–589. Reproduced under the terms of creative common license (CC-BY 3.0). Copyright (2012) Elsevier.

Another technique of graphene production is by reducing graphene oxides. Graphene oxide can be produced by the oxidation of graphite using concentrated acids and strong oxidants, as the graphite oxide exfoliates more readily by thermal treatment or sonication than graphite (Edwards and Coleman, 2013). Graphene oxide is highly insulation and hence is highly desired to reduce completely to regain the electrical properties of the graphene. Graphene oxide can be reduced at relatively low temperatures using specific reducing agents such as sodium hypochlorite, sodium hydrosulphite, and sodium borohydride. After reduction, the material is generally termed “reduced graphene oxide” or “functionalised graphene” with degraded electrical performance compared to pure graphene. It will always contain some defects even after complete reduction.

Bottom-up approaches

Bottom-up approaches include chemical vapour deposition (CVD), epitaxial growth, laser-assisted synthesis, pyrolysis, and so on. CVD-based techniques were widely adopted, especially in industries, to produce large-area high-quality graphene films on top of metallic surfaces like Cu, Ni, Pt, and Al. Among them, Cu is preferred because of the low solubility limit of carbon in Cu. The primary mechanism of CVD growth of graphene is the thermal decomposition of hydrocarbon on a heated transition metal surface. In metals with high carbon solubility, such as Ni, carbon will diffuse or dissolve into the heated substrate. The dissolved carbon will segregate to the surface to create graphene sheets when the substrate cools. For metals with low carbon solubility, such as Cu, carbon atoms will nucleate and laterally extend around the nucleus to form graphene. The major challenge associated with CVD growth is the mismatch in the thermal expansion coefficient of the metallic substrate with that of graphene results in wrinkles and other defect formations. So, materials such as Mo with similar thermal expansion to that of graphene were also recently reported.

The CVD based high-quality single-layer graphene has been developed on commercially available Cu foil of 400 cm² (Polat *et al.*, 2015). The Cu substrate was annealed at 1035°C for half an hour before the growth. Methane (CH₄) was sent at a partial pressure of 285 mTorr at 25 sccm, along with hydrogen, into the growth chamber. Catalytic decomposition of methane takes place on the Cu surface to form C_xH_y. The Cu surface can be either undersaturated, saturated, or supersaturated based on the parameters of Methane flow, pressure, temperature, and hydrogen partial pressure. Under optimised parameter conditions, uniform and complete surface coverage can be achieved (Li *et al.*, 2010). After the deposition, the sample was suddenly cooled to room

Table 1 Comparison between various graphene production techniques

	<i>Fabrication technique</i>	<i>Advantages</i>	<i>Disadvantages</i>
Top-down	Mechanical cleavage	● Simple and inexpensive technique ● No need for sophisticated instruments ● Compatible with various multi-layered sources ● Good for demonstrations	● Not suitable for mass production ● Dimensional restrictions based on initial crystal
	Liquid phase exfoliation	● Simple and inexpensive technique ● Faster compared to mechanical cleavage	● Not high yielding ● Dimensional restrictions based on initial crystal
	Graphene oxide reduction	● Large area and industrial production ● Inexpensive ● Can produce reduced graphene oxides with tunable semiconducting properties	● Dimensional restrictions based on initial crystal ● Degraded electrical performance due to incomplete reduction
Bottom-up	CVD	● Large area and industrial production ● It can be easily transferred into any substrate	● The quality of graphene will be affected during the transfer
	Epitaxial growth	● Large-area single and few-layer graphene ● Growing directly on an insulating substrate such as SiC ● Good for quality device fabrication	● Size limited by SiC surface ● Very expensive to produce and need specific instruments ● Not suitable for flexible devices

temperature. It is not necessary that the growth substrate needs to be the target substrate, and the film can be subsequently transferred to flexible substrates such as PET and PEN. One technique is to drop cast photoresist over the graphene on Cu and subsequently etched the Cu using FeCl_3 solution. The graphene was released to the target substrate by removing the photoresist by treating it with temperature or alcohol (Polat *et al.*, 2015). Hot lamination technique can directly transfer CVD-grown graphene to PVC. The graphene on 4 in. Cu was placed in contact with PVC and inserted into a hot lamination roll at 125°C , which resulted in the PVC sticking to the graphene holding Cu, followed by etching the Cu using FeCl_3 solution (Núñez *et al.*, 2017b). Dato *et al.* proposed a substrate-free CVD of graphene nanosheets using ethanol on an atmospheric pressure microwave plasma reactor (Dato *et al.*, 2008). The technique favours continuous large-area graphene production.

Epitaxial graphene growth on hexagonal phase substrate such as SiC is an alternative approach to obtaining high-quality graphene. The thermal decomposition of SiC under ultra-high vacuum at high temperature ($> 1000^\circ\text{C}$) results in the sublimation of Si, leaving a layer of carbon on the surface (Tetlow *et al.*, 2014). Compared to CVD, where carbon is supplied in the form of gas with the heated substrate acting as the catalyst, in epitaxial growth, the substrate is thermally decomposed to form a layer of carbon already present in the substrate. The growth of single-layer graphene over SiC is more challenging than CVD and more expensive when comparing hexagonal phase SiC with Cu foil. Epitaxial graphene growth is preferred for wafer-based applications such as electronic transistors and devices, where the graphene must not be removed from the underlying substrate.

Table 1 summarises the advantages and disadvantages of various graphene production techniques. Choosing the best approach among them is impossible since each method will have strengths and shortcomings that complement those of other techniques. For instance, graphene oxide reduction works well for large-scale, low-cost industrial manufacturing, but the quality degrades. The best-quality graphene will be epitaxial, but it is expensive to produce in large quantities.

Touch Sensor Applications

Touch sensors find application in simple day-to-day interfacing circuits to sophisticated wearables and robotic e-skins (Dahiya *et al.*, 2019a). A touch sensor converts a physical touch using a sensing element into an electrical signal (Nair *et al.*, 2021b). Based on the position of the sensing element, the touch sensing can be proximity sensing (distance > 0) or hover touch, normal touch sensing (at 0 positions), or pressure sensing (distance < 0) (Vu *et al.*, 2021). There are multiple sensing mechanisms; capacitive, resistive, or self-powered techniques are popular among them (Nair *et al.*, 2019).

Capacitive Touch Sensing

Capacitance-based sensors are widely reported because of their features such as low cost, quick response, low power consumption, thermal stability, flexible nature of the electrodes and simple readout electronics (Dahiya *et al.*, 2015; Nair *et al.*, 2019; Ntagios and Dahiya, 2022; Nikbakhtnasrabadi *et al.*, 2022; Nair *et al.*, 2020b; Hosseini *et al.*, 2022; Kumaresan *et al.*, 2022a; Kumaresan *et al.*, 2021). It works by sensing a variation in the effective capacitance of the device with a physical touch (Kumaresan *et al.*, 2022a). Capacitive sensing can be either surface or projected capacitive based on the mechanism. A conductive large-area electrode with a dielectric layer on top is employed for surface capacitive, with symmetrical AC signals supplied to each of its four corners. Touching the top dielectric with one's hand alters the current distribution across it due to the establishment of a dynamic

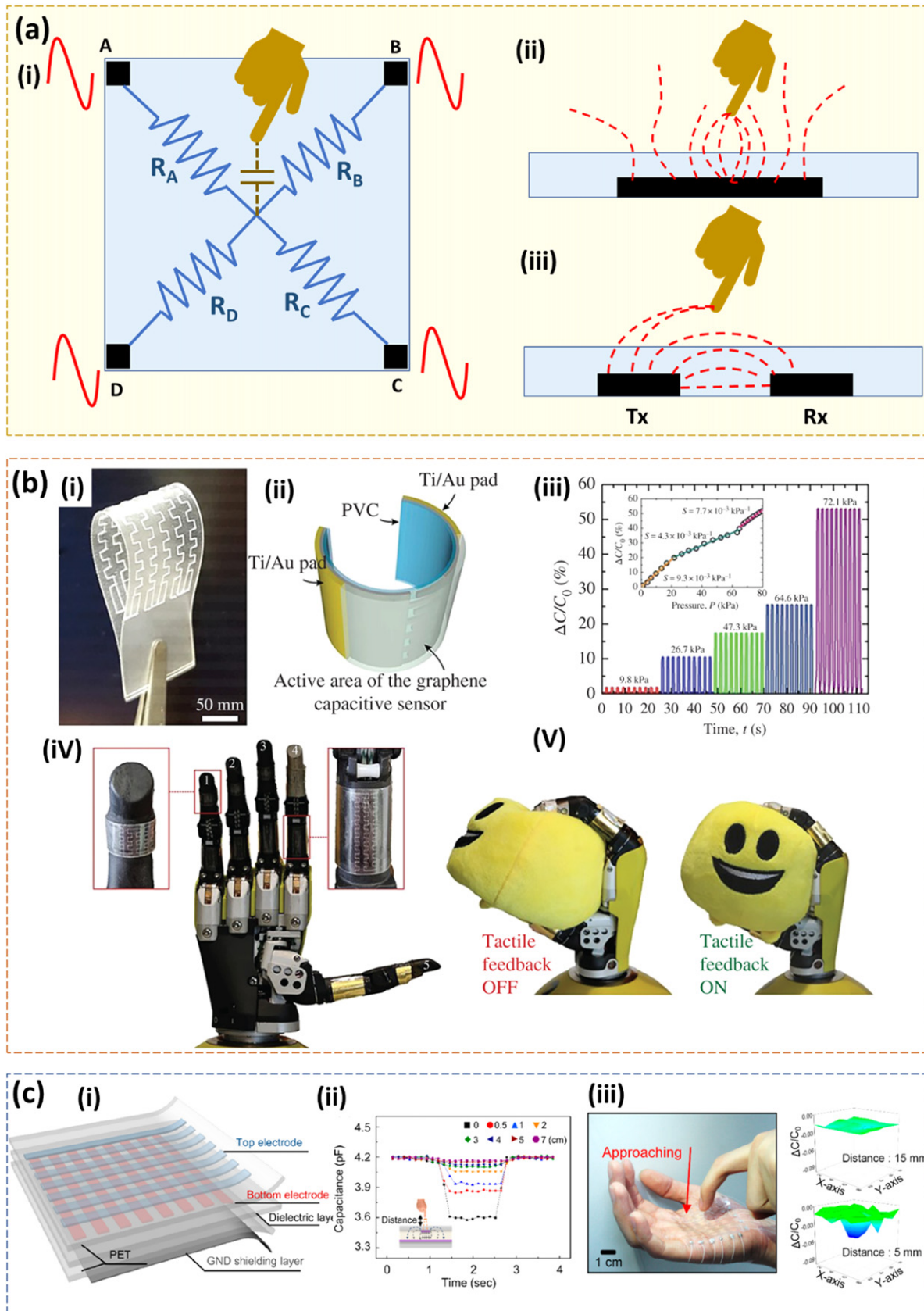


Fig. 7 Various capacitive touch sensors. (a) Mechanism of (i) surface capacitive, (ii) self, and (iii) mutual projected capacitive touch sensing. (b) Large area self-capacitance-based graphene tactile sensors: (i) photograph, (ii) structure, and (iii) performance of the graphene touch sensor.

(iv) eSkin with capacitive sensors integrated into a robotic hand and (v) functioning as tactile feedback for grabbing soft objects. (c) Transparent and flexible mutual capacitance-based graphene touch sensor: (i) Schematic diagram, (ii) performance with touch and proximity, and (iii) 3D measurement of approaching object and corresponding surface mapping of the touch sensor. Reproduced with permission from Kang, M., Kim, J., Jang, B., *et al.*, 2017. Graphene-based three-dimensional capacitive touch sensor for wearable electronics. *ACS Nano* 11, 7950–7957. Copyright (2017) American Chemical Society. Núñez, C.G., Navaraj, W.T., Polat, E.O., Dahiya, R., 2017b. Energy-autonomous, flexible, and transparent tactile skin. *Advanced Functional Materials* 27, 1606287. Reproduced under the terms of creative common license (CC-BY 4.0), John Wiley & Sons.

capacitance, which draws additional current from the corners, with the corner nearest to the contact point exhibiting the most fluctuation due to its low resistive path. Based on these current modulations, the touch position can be determined (Fig. 7 (a i)). The surface capacitive sensing method does not support multipoint touch sensing but is more suitable for large-area sensors with high durability (Dahiya and Valle, 2013).

A more widespread approach is projected capacitive sensing, which can be further differentiated into self (Fig. 7 (a ii)) and mutual capacitive sensing (Fig. 7 (a iii)). Self-capacitive sensors work based on the mechanism of change in capacitance of an electrode with respect to the ground or the human finger/stylus. A parallel plate capacitive sensor, comprising of two conducting electrodes separated by a dielectric, is a typical example in which, when pressed, the relative capacitance changes according to the compression of the dielectric material in between (Kumaresan *et al.*, 2021). Such sensors are superior for pressure-sensing applications, especially in hard-touch regimes. The amount of charge transferred from one electrode to another is measured by mutual capacitance because the amount of transferred charge differs under touch conditions due to electric field modulations. This configuration is widely adopted in modern mobile phone touch technologies, especially as row-column arrangements to identify a specific touch position and is suitable for normal and soft touch identifications. Given the presence of fringe electric field domination, mutual capacitive sensing could also be employed for proximity sensing.

A parameter termed sensitivity, defined as the change in capacitance (or other parameters based on the mechanism) to applied pressure, is often used to compare the performance of the capacitive sensors at various pressure regimes (Hosseini *et al.*, 2022). Sensitivity (S) is defined as:

$$S = \frac{\Delta C/C_0}{\Delta P} \quad (4)$$

Where ΔC is the change in capacitance ($C - C_0$), C_0 is the initial capacitance or capacitance without any touch, and ΔP is the differential pressure that caused the change in the capacitance.

A graphene-based transparent tactile skin, as a flexible energy autonomous e-skin application, is shown in Fig. 7 (b) (Núñez *et al.*, 2017b). The CVD-grown monolayer graphene on Cu foil was transferred onto a PVC substrate by a hot-roll technique at 125 °C and patterned using a simple mechanical blade cutter. The sensor works based on the mechanism of self-capacitance, consisting of the interdigitated electrode structure, with one of the electrodes energised while the other was grounded for the measurements. It detected a minimum pressure of 0.11 kPa up to 80 kPa, with a sensitivity of 4.3 Pa⁻¹, for comprehensive range pressure sensing. With less than 5% optical absorbance, the sensor may indeed be transformed into an self-powered device by adding photovoltaics beneath the sensor to gather light that passes through the sensor. The capacitive sensor response was effectively employed as tactile feedback in an artificial hand, allowing manipulation of stiff and soft items of various forms.

Another example is the 8 × 8 sensor array developed for contact and non-contact touch detection. The sensor consists of triple-layer graphene on PET substrate as electrodes and an acrylic dielectric in between (Fig. 7 (c)). (Kang *et al.*, 2017) An additional third grounded layer at the bottom makes the sensor insensitive to the nature of the surface where the sensor was installed. In this case, the graphene layer is doped with bis(trifluoromethane) sulphonamide to improve the conductivity up to 320 ohm/sq. The sensor works based on the mutual capacitance between the electrodes, with a 14.5% capacitance variation when touched and almost insensitive to humidity and temperature variations. The sensor is also able to detect proximity and hover touch.

Resistive Touch Sensing

Resistive sensors work based on the voltage sampling at the touch point to extract the location of the touch. Basically, this type of sensors consists of two conducting layers separated using an insulating spacer in between. Two contacts are attached to the individual conductive layers at orthogonal positions. When touched, the distance between the individual layers reduces, thereby reducing the resistance between the layers and finally, they contact with each other. Then a DC voltage will be applied to one of the layers, and the voltage induced between the two contacts of the other layer is measured to understand the coordinate of the touch. In general, a resistive sensor is insensitive to the nature of the touch element, even if it works equally with an insulating rod, a human finger with or without insulating gloves, or the stylus. The resistive sensor cannot support multiple touch detection as separating the individual touch voltage signals is arduous.

An example of graphene based touch sensor includes the ultra-sensitive resistive sensor with a foam-like structure fabricated using laser-scribed graphene (Tian *et al.*, 2015). The sensors exhibits a sensitivity of 0.96 kPa⁻¹ for a wide range of pressure, from 0 to 50 kPa (Fig. 8 (a)). The laser-scribing helps to induce a V-shaped microstructure to the graphene surface. This microstructure increases the interelectrode spacing between the graphene layers, which finally helps to enhance the sensor performance. The sensor responds faster, within 0.4 ms, even at higher pressure regimes. Figure 9a shows the structure of the sensor and its

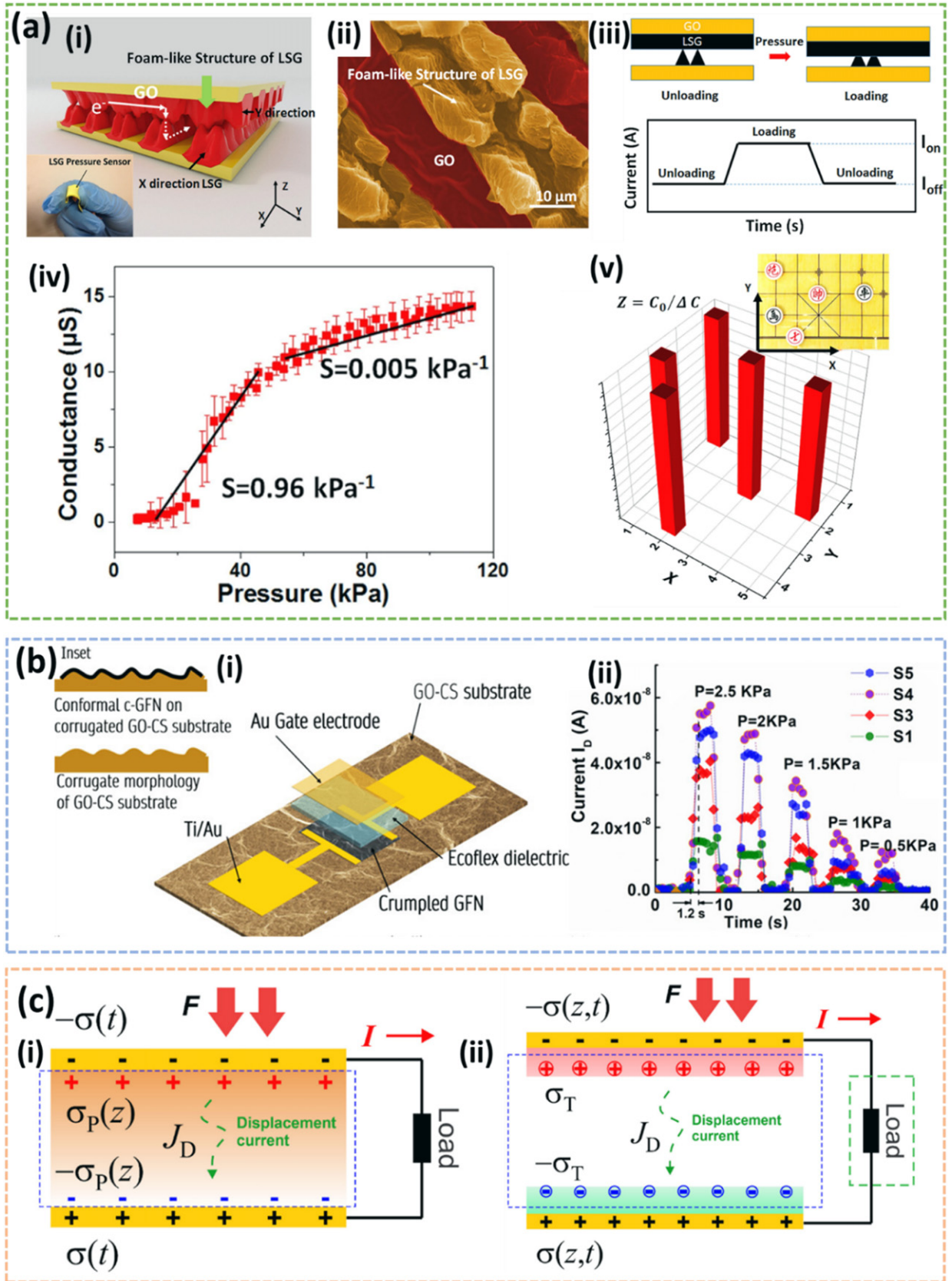


Fig. 8 (a) The laser-scribed graphene sensor: (i) The schematic of the structure of the graphene sensor with the inset showing a photograph of the sensor. (ii) microstructure of the laser-scribed surface. (iii) Schematic representation of the sensing mechanism and the corresponding

variation in the current. (iv) The static pressure response and (v) the working of a 5×4 sensor array. (b) PRESSFET: (i) Schematic representation of PRESSFET with top-gated architecture and corrugated morphology (inset). (ii) Variation in the device current with different pressure inputs. (c) Mechanism of self-powered touch sensors. (i) Piezoelectric nanogenerators and (ii) Triboelectric nanogenerators. Reproduced from Tian, H., Shu, Y., Wang, X.F., *et al.*, 2015. A graphene-based resistive pressure sensor with record-high sensitivity in a wide pressure range. *Scientific Reports* 5, 8603. Reproduced under the terms of creative common license (CC-BY 4.0), Copyright (2015) Springer nature. Paul, A., Yogeswaran, N., Dahiya, R., 2022b. Ultra-flexible biodegradable pressure sensitive field effect transistors for hands-free control of robot movements. *Advanced Intelligent Systems*. 4, 2200183. Reproduced under the terms of creative common license (CC-BY 4.0). Copyright (2022) John Wiley & Sons. Sriphan, S., Vittayakorn, N., 2022. Hybrid piezoelectric-triboelectric nanogenerators for flexible electronics: Recent advances and perspectives. *Journal of Science: Advanced Materials and Devices* 7. Copyright (2022) Elsevier.

performance. Another interested work uses stretchability of graphene to create a resistive strain sensor using an elastomer-graphene carbon composite (Kumaresan *et al.*, 2022b).

Pressure Sensing Field Effect Transistors (PRESSFETs)

PRESSFETs combine pressure sensors and transistors with high-pressure sensitivity and switching capabilities (Paul *et al.*, 2022b). Crumpled graphene flakes have been used as the semiconducting channel, with Ecoflex as the dielectric that can deform under pressure on the graphene oxide-chitosan composite substrate (Fig. 8(b)). The usage of graphene is restricted for transistor applications due to its zero-band gap. However, the crumpled structure morphology helps to open a direct band gap, which enhances the FET performance. Owing to crumpled morphology of graphene, significant thickness variation of the soft dielectric material can be observed with even slight external pressure, which modulates the ON state drain current. As a result, the PRESSFETs offer high sensitivity with a low detection limit. Due to the combination of sensor and transistor capabilities, the PRESSFET device may deliver signal amplification, a higher signal-to-noise ratio, and simpler sensor frontend electrical circuitry. The heterogeneous integration of graphene sensors with other devices based on Si technology is extensively researched for high-performance applications (Christou *et al.*, 2023; Dahiya *et al.*, 2022) and PRESSFETs too may benefit from the same.

Self-Powered Touch Sensing

Self-powered touch sensing can be achieved by using energy-harvesting methods like piezoelectricity and triboelectrification, which can convert mechanical deformations into electrical signals (Min *et al.*, 2023; Min *et al.*, 2021). These sensors benefit from not requiring any large, bulky external power supply (Mukherjee *et al.*, 2021).

Piezoelectric materials are those that polarise when mechanical pressure is applied and are reversible (Sriphan and Vittayakorn, 2022; Deswal *et al.*, 2022). The property of piezoelectricity can be utilised for force and pressure sensing applications. (Khandelwal *et al.*, 2023) Fig. 8 (c i) demonstrate the mechanism of piezoelectric force sensing. Due to the fact that non-centrosymmetric materials typically display piezoelectricity, graphene is not an ideal material for piezoelectric properties. But, due to the high carrier mobility and conducting properties, graphene can be a perfect electrode material that can make contact to transport the generated carriers from other piezoelectric materials. An example of piezoelectric nanogenerator (PENG) includes the stretchable and transparent device developed by sandwiching a layer of polymeric piezoelectric material, poly(vinylidene fluoride tri-fluoroethylene) (P(VDF-TrFE)), between CVD grown graphene transferred on to PDMS (Lee *et al.*, 2013). The PENG was highly sensitive, even responding to acoustic and airflow.

Triboelectric nanogenerators (TENG) utilise the triboelectrification phenomena, where a material gets charged after making mechanical contact with another material and then separated (Khandelwal and Dahiya, 2022; Sriphan and Vittayakorn, 2022) Fig. 8 (c.ii) demonstrate the mechanism of triboelectric force sensing. A notable example is the stretchable and transparent TENG, realised using wrinkled graphene with a plastic spacer (Kim *et al.*, 2014). Under vertical compressive stress of 9.88 N, the device made of single-layer graphene electrodes displayed an output voltage of 5 V and a current density of $0.5 \mu\text{A}/\text{cm}^2$. Although not extensively explored for touch sensing, these technologies are promising for the future as self-powered transparent pressure sensors and energy harvesters since they can efficiently transform mechanical energy into electrical energy. The advanced optoelectronics that graphene can provide will complement to make these devices transparent and flexible.

Conclusion and Future Perspectives

This article provided an overview of graphene, its various properties and how they may be utilised to manufacture touch sensors. Due to its high carrier mobility, transparency, flexibility and low cost, graphene is also an excellent substitute for ITO and other transparent conductors for touchscreen applications. Due to its extremely high carrier mobility, graphene also has tremendous potential for high-speed optoelectronic devices. Because the performance of the film is strongly dependent on the synthesis mechanism, the development of synthesis techniques is equally critical. In recent years, there has been immense progress in synthesis techniques, growing substrates, transferring, and patterning methods that made graphene handling much more feasible

and cost-effective. The CVD synthesis of graphene made it possible to produce decent quality over a large area. Further, the transferring techniques, along with doping, have enabled the development of efficient, flexible transparent conductors. Being single atomic thickness, the handling of graphene is complicated as it is more susceptible to scratches. Proper packaging is critical, but encapsulating without compromising graphene quality is another difficulty.

There have been considerable advances in the past few years in graphene-based touch sensing, especially in terms of morphological tuning of graphene and its derivatives, making composites with other materials to enhance the device performance, new sensor architectures and constructive enhancements in fundamentals related to the sensing techniques, and high-performance sensors. The high sheet resistance of graphene is a challenge for capacitive sensors as it could increase the time delay. Such issues could be addressed by proper doping and structural modifications. Graphene-based piezoelectric and triboelectric nanogenerators could be explored further as self-powered sensors that could drive wearable electronics in future, especially for large-area implementations. Graphene can be easily modified and combined with other materials that open new horizons in sensing and performance improvement. The excellent mechanical strength, environmental stability, thermal conductivity, and adaptability of graphene, which are not extensively utilised in sensing, can be further explored and incorporated to make multifunctional intelligent sensors that can sense more than touch. More fascinating efforts and extensive study into the desired applications of highly flexible, conductive, transparent, and cost-effective graphene in future touchscreen smart nanodevices are therefore considered essential, and more multi-disciplinary efforts are required for timely commercialization.

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Disposable Pressure Sensors

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Abstract

The “tsunami of electronic waste (e-waste)” that has hit the world left us with a surprising environmental cost to be reckoned with – an obsolete digital dumpsite of 53.6 million tonnes. With such an enormous amount of digital dumpsite existing with its fate being “simply unknown”, the problem is exasperated as during the manufacture of electronics, a significant amount of chemical waste is generated as by-products. Sustainable fabrication of degradable pressure sensor devices can be achieved by consciously choosing renewable starting materials and applying low cost and simple fabrication process which will lead to lesser wastage, less energy and lesser use of rare earth materials. Thus, a step-change towards understanding the chemistry of materials, their degradation pathways, ecodesign and fabrication of sensor devices with easy disassembly steps for their reuse or recycling is the need of the hour towards closing the loop on waste generation.

Key Points

- Common chemistries and engineering strategies to select starting biodegradable materials for pressure sensor devices are presented.
- Recent progress in various biodegradable pressure sensors is summarized.
- End of life-cycle of degradable pressure sensor devices is discussed.

Introduction

The emergence of transient electronics has offered the world a potential route to reduce the enormous amount of untreated electronic waste (e-waste) that is being generated worldwide. Transiency in simpler words means creating systems with the fate of completely or partially dissolving, degrading, or disappearing in their surroundings as their utility period ends. The essence of this waste-free technology lies in the usage of biodegradable, biocompatible and sustainable materials in fabricating electronic devices (Jamshidi *et al.*, 2022). In the last decade, an exponential increase in the use of these materials covering almost every facet of science and engineering such as medical tools, drug delivery, food packaging and implantable devices, has been seen (Manjakkal *et al.*, 2021; Yalagala *et al.*, 2022; Aliyana *et al.*, 2022; Chakraborty *et al.*, 2022; Beniwal *et al.*, 2023; Paul *et al.*, 2022; Dahiya *et al.*, 2022; Dervin *et al.*, 2021; Bhattacharjee *et al.*, 2019; Kafi *et al.*, 2020).

Using transient electronics to develop bio-inspired electronic skin (e-skin), which mimicks a difficult canvas like human skin is quite a difficult engineering challenge in itself and considerable research is being conducted owing to its applications in wearable healthcare and implantable devices, robotics, and human-machine interfaces (Soni and Dahiya, 2020; Dahiya *et al.*, 2019; Liu *et al.*, 2022a,b; Neto *et al.*, 2022; Ozioko and Dahiya, 2022). In pursuit of giving the e-skin the ability to respond to contact force, a wide variety of pressure sensors with different sensing mechanisms have been explored.

Pressure sensors convert mechanical stimuli or any deformation caused due to external pressure or force applied on the object to assessable electronic signals. There are mainly four types of transduction mechanisms of pressure sensors, viz., resistive, capacitive, piezoelectric, and triboelectric which are briefly summarized in Table 1 (Pierre Claver and Zhao, 2021; Meng *et al.*, 2022; Dahiya and Valle, 2013). These sensing mechanisms vary from one another in terms of design geometry, materials used and the output signals. The physical and chemical characteristics of the materials used to develop these sensors affect their performance to a greater extent. Traditional pressure sensor materials provide considerable sensitivity, but often they are made of non-degradable and sometimes toxic materials (Shi *et al.*, 2022a). These materials aggravate the global challenges such as electronic waste and as result sustainable, and eco-friendly materials are currently being explored as an active sensing material, substrate and encapsulant to develop degradable sensor devices (Hosseini *et al.*, 2020a; Chakraborty *et al.*, 2022). The “greenness” associated with these low-cost, and renewable materials could mitigate the environmental and social damage of e-waste to a greater extent. However, the complexity surrounding biodegradable sensors technology cannot be overlooked as it is quite challenging to have all the components of sensors to be made from biodegradable materials. This chapter will introduce commonly used inexpensive, sustainable, bioderived and biodegradable material which have been used in developing fully disposable pressure sensor devices.

Table 1 Types of pressure sensor devices

Type	Resistive	Capacitive	Piezoelectric	Triboelectric
Structure	Two vertical electrodes separated by conductive sensing material which is either elastic or semi conductive	A dielectric layer sandwiched between two electrodes	Two vertically aligned electrodes separated by a piezoelectric material	Most widely used is the contact separation mode comprises of dielectric-dielectric or metal to dielectric contact.
Principle	When pressure is applied, the conductivity or density of the sensing conductive material changes, affecting the resistance (R) of the sensor device. The R can be controlled following the equation: $R = \frac{\rho l}{A_1}$	The capacitance can be increased by changing the dielectric constant or decreasing the distance between the electrodes. $C = \frac{\epsilon_{air} \epsilon_r A_2}{d}$	The application of external pressure brings the deformation in oriented non-centrosymmetric crystal structures resulting in spatial separation of positive and negative charges, which leads to the formation of charges on the cathode and anode	A triboelectric pressure sensor convert a mechanical signal to an electrical signal by coupling contact electrification with electrostatic induction.
Advantages	simple structure, easy to fabricate, simple readout mechanism, high signal-to-noise ratio, high sensitivity in a low-pressure area	Can non-contact testing, simple structure, easy to fabricate, simple readout electronics, good sensitivity, stability, shorter response times	can operate without external power, highly suitable for dynamic pressure sensing	inexpensive, simple structure, and can operate without external power
Limitations	demanding power consumption, hysteresis, an high drift over time	Vulnerable to affected by surroundings	Measurements are temperature sensitive, high drift in response over time, susceptible to environmental factors	Device susceptibility to environmental factors

ρ = resistivity, l = length, A_1 = area of the conductor, ϵ_{air} = permittivity of air, ϵ_r = relative permittivity of the dielectric layer, d = distance between the two electrodes, and A_2 = covered area of the two electrodes.

Criteria of Selection of Degradable Materials for Sensor Devices

The first important requirement of next generation electronics is using self destructive materials which, when discarded in the natural environment, degrade to form useful or non-toxic by products such as carbon-dioxide, water etc. Secondly, during the operational cycle of the sensor device, the materials should not undergo any harmful reaction to the surrounding environment and thirdly, the materials should not compromise the performance of the device during its operational lifetime. The toxicity and carcinogenicity of these materials can be determined by studying their degradation, corrosion, and dissolution rate by creating similar ambient temperature, pressure and salinity in laboratories (Wang *et al.*, 2022b; Shin *et al.*, 2022).

Ideally, a biodegradable or disposable sensor should consist of fully degradable components. However, till date there are only few examples of completely biodegradable sensors and the materials explored in these reports are summarized in Table 2. Though the use of degradable and biocompatible materials is an essential step towards alleviating e-waste problem, the performance of these device can not be compromised as otherwise they will not be useful for target applications. In this regard, physical characteristics of the materials such as Young's modulus, electrical conductivity and water permeability should also be given equal importance while selecting the material (Pan and Lee, 2021).

In this chapter, biodegradable materials are classified into two categories, namely, hydrolysable inorganics and polymers (natural as well as synthetic), and their role in sensor devices which preserve their characteristics and reliable function or performance in the targeted application.

Hydrolysable Inorganics

Many elements such as Mg, Zn, Cu, Fe, Si etc and their oxides, owing to their satisfactory electrical properties, biocompatibility, good processability, have been used as electrode in disposable pressure sensor devices. These elements and their oxides are considered unharmed as when present in their cation form they can be easily absorbed by human body or taken up by plants as trace and micro nutrients respectively. Hence, their dissolution rate plays a very important role and it can be calculated either via theoretical and empirical models or by experimental studies. The dissolution rate of most of these inorganics has been found higher in acidic conditions than that in neutral and alkaline conditions (Wu *et al.*, 2020). Recently, silicon and magnesium are declared critical raw materials by European Commission (Pommeret *et al.*, 2022) and the biophysical malfunctions caused by copper has raised concerns among researchers.

The dissolution mechanism of nanoparticles (NPs) is still a subject of debate among scientists despite extensive works that are being carried out. Being quite smaller in size as compared to their bulk counterparts, the nanoparticles offer larger surface area and hence higher sites for interaction with solvent molecules and thus they exhibit faster dissolution. Thus, the nanosized particles exhibit higher toxicity. For instance, AgNPs and AuNPs accumulate liver and spleen. Pure graphene has been documented to induce a subchronic inflammatory response in a study carried out on mice. Furthermore, it provokes autophagy accompanying apoptosis via mitochondria damage, and carbon nanotubes lead to granulomatous inflammation in the lung and multiple organs (Wu *et al.*, 2020).

Polymers

Undoubtedly, the hydrolysable inorganic materials have merit of having excellent electrical properties. The potential toxicity associated with them could exceed the allowable dosage to human system and environment and hence can not be ignored. Thus, completely/partially replacing them with organic materials such as polymers could be a biosafe solution. In the category of conductive polymers, polythiophene and poly(3,4-ethylenedioxythiophene) are considered as relative safer polymers. There is certain degree of toxicity reported for some polymers such as polyaniline and polypyrrole which are considered degradable but not safe for the ecological system. Besides these, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) has been nowadays used as a biocompatible conductive polymer owing to its high electrical conductivity, mobility and stability (Zare *et al.*, 2019; Zhang *et al.*, 2022b; Soni *et al.*, 2020; Bhattacharjee *et al.*, 2020; Manjakkal *et al.*, 2020) and the biocompatibility of the polymer has been studied in detail on several different cell lines. Moreover, the properties of the polymers can be improved by tuning their structure. For instance, conducting oligomers of pyrrole and thiophene were connected via ester linkage and attributed to the degradable nature of esters, the resultant conductive polymer exhibited faster degradation rate. This interesting and degradable polymer under atmospheric conditions can be disintegrated in to many smaller oligomers which act as food for macrophages (Soni *et al.*, 2020).

The other two main components of a sensor device are substrate and encapsulant. Substrate play a dual role of providing mechanical support to the device as well as it controls and aids the rate of disintegration of the device during the degradation period. Encapsulants on the other hand determines the functional life time period of the sensor device as they decrease the rate of water diffusion toward the main active circuit. Table 2 lists the commonly used degradable, biocompatible and bioderived polymers as a substrate/encapsulant for developing disposable sensors (Koh and Khor, 2022).

Degradation Mechanism

The degradation mechanism of the polymers can be broadly categorised into two types: hydrolysis and oxidative. In the case of enzyme mediated acid catalysed ester hydrolysis, the prominent enzymes involved in degradation process are proteases, esterases and glycosidase. Usually, in case of enzyme mediated degradation, owing to their large size they are unable to penetrate materials and thus only induce surface degradation. On the other hand, to catalyse hydrolysis rate, the catalyst present in the environment such as H^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , OH^- , HCO_3^- , Cl^- , $H_2PO_4^{2-}$ and SO_4^{2-} aids the hydrolysis. The rate of degradation is directly proportional to the rate of diffusion of salt into the polymers, which is affected by the hydrophilicity of the polymer and number of hydrolysable functionalities linked with the polymer. The temperature, morphology, density and chemical composition of the polymer are some other factors which also affect the hydrolysis rate. The presence of ester, amide, imide, anhydride, carbonate moieties or in simpler words groups containing $-C=O$ bonds linked to heteroatoms such as oxygen, nitrogen etc. are susceptible to easy chemical/enzymatic hydrolytic degradation.

Oxidative degradation occurs in three stages: Initiation, propagation and termination and generally involves formation of radicals. It occurs to the functional groups which involves allylic, ethers, phenols, alcohols, aldehydes, and amines. Moreover, a certain amount of threshold energy (ranging from 30 to 90 kcal) known as triggered energy in form of heat or light is required to aid the oxidative degradation of polymers (Chen *et al.*, 2022). However, the degradation studies of most of the polymers are still incomplete. In this regard, terming them as biodegradable need to be critically revisited and confirmed authoritatively.

Strategies for Pressure Sensors With Outstanding Characteristics

The evaluation of the disposable pressure sensors' performance can be classified into various factors, including their sensing performance, range of working, stability, response/recovery time, to name a few. Researchers have made remarkable attempts to improve these parameters. Sensitivity (S) of the pressure sensors can be expressed as $S = d(\Delta A)/dP$, where ΔA is the change of either capacitance (C) or resistance (R) or current (I) for capacitive, resistive and piezoelectric mechanism, respectively, while ΔP is the pressure applied on the sensor. The attempts to enhance the sensitivity included approaches such as using active biodegradable/natural sensing materials with conductive property as well as processes such as introducing the active layer to achieve microstructures or developing multiscale structures to exploit the contact under different pressures. As for the low hysteresis and fast response and recovery time, some effective methods are designing or selecting materials with low viscoelasticity and fast deformation or constructing conductive channels. The stability and reproducibility of the sensor can be achieved by having a good connection between the sensing layers (for a multi-layered structure) or a strong connection between the sensing layer and the electrodes. Another way is to select materials with a negligible thermal expansion effect (Shi *et al.*, 2022b; Li *et al.*, 2018). To that extent, the following section reports various materials that have been used for different pressure sensor mechanisms (Table 2), as well as briefly describes the latest advances for each disposable pressure sensor mechanism.

Recent Advances Made in Various Types of Pressure Sensor Devices

Capacitive

Capacitive pressure sensors are commonly adopted sensing devices in wearable/implantable electronics, robotics, aerospace, automotive and marine applications, owing to their outstanding applications, simple structure, simple readout electronics and low-cost

Table 2 Summary of materials for disposable pressure sensors.

	Materials	Mechanism
Sensing layer	Biodegradable polymers: polyvinyl alcohol (PVA) (Durukan <i>et al.</i> , 2022), poly Lactic-co-Glycolic Acid (PLGA) (Khalid <i>et al.</i> , 2019) polycaprolactone (PCL) (Khalid <i>et al.</i> , 2019), poly (glycerol sebacate) (PGS) (Boutry <i>et al.</i> , 2018)	Capacitive
	Natural polymers: chitosan (Song <i>et al.</i> , 2022), cellulose tape (Koivikko <i>et al.</i> , 2020)	
	Carbon-based: graphene (Kou <i>et al.</i> , 2019),	
	Elastomers: eco flex (Hou <i>et al.</i> , 2019), Poly (sebacoyl diglyceride) (PSeD)-graft-2-ureido-4 [1 H]-pyrimidinone unit (PSeD-U) (Chen <i>et al.</i> , 2020), porous polydimethylsiloxane (PMDS) (Amit <i>et al.</i> , 2019; Bilent <i>et al.</i> , 2020; Liu <i>et al.</i> , 2019)	Resistive
	Natural polymers: silk fibroin (SF) (Chao <i>et al.</i> , 2021), carbonized silk nanofibers (Wang <i>et al.</i> , 2017b), cross-linked collagen fibers (CCF) (Zhang <i>et al.</i> , 2022a), collagen aggregates (Wang <i>et al.</i> , 2020b), chitosan (Song <i>et al.</i> , 2022), bacterial cellulose (Chen <i>et al.</i> , 2020; Wei <i>et al.</i> , 2021), cellulose nanocrystals (CNC) (Zhao <i>et al.</i> , 2019), cellulose fibers (Long <i>et al.</i> , 2021), sunflower pollen microcapsules (SFP) (Wang <i>et al.</i> , 2017a), tissue paper (Guo <i>et al.</i> , 2019), cotton fabric (Liu <i>et al.</i> , 2017)	
	Carbon-based: reduced (r)GO (Zheng <i>et al.</i> , 2021; Ma <i>et al.</i> , 2022), graphene (Xiao <i>et al.</i> , 2018; Huang <i>et al.</i> , 2019; He <i>et al.</i> , 2019), CNT (Lee <i>et al.</i> , 2019; Zhao <i>et al.</i> , 2020; Wang <i>et al.</i> , 2017a; Wu <i>et al.</i> , 2018; Liu <i>et al.</i> , 2017; Sun <i>et al.</i> , 2018), MXene (Chao <i>et al.</i> , 2021; Guo <i>et al.</i> , 2019; Zhang <i>et al.</i> , 2022a; Zhuo <i>et al.</i> , 2019; Chen <i>et al.</i> , 2019b; Ma <i>et al.</i> , 2018)	
	Conductive polymers: PANi (Zheng <i>et al.</i> , 2021; Huang <i>et al.</i> , 2019),	
	Elastomers: PDMS (Shi <i>et al.</i> , 2018; Wang <i>et al.</i> , 2017a; He <i>et al.</i> , 2019; Tang <i>et al.</i> , 2021; Sun <i>et al.</i> , 2018; Wang <i>et al.</i> , 2018)	Piezoelectric
	Natural polymers: Silk (Joseph <i>et al.</i> , 2018; Liu <i>et al.</i> , 2019), Chitosan (Hosseini <i>et al.</i> , 2020b), PLLA (Curry <i>et al.</i> , 2018)	
	Natural Polymers: : CNC (Wang <i>et al.</i> , 2022a), crepe cellulose paper (CCP) (Chen <i>et al.</i> , 2019a), Starch paper (Zhu <i>et al.</i> , 2018), methylcellulose (MC) (Wang <i>et al.</i> , 2022a), Nitrocellulose (NCM) (Chen <i>et al.</i> , 2019a)	Triboelectric
	Biodegradable polymers: PLGA (Peng <i>et al.</i> , 2020), PVA/sucrose/glycerol (PSG) (Durukan <i>et al.</i> , 2022),	
	Natural: human skin (Zhu <i>et al.</i> , 2018),	
	Elastomers: PDMS (Ma <i>et al.</i> , 2017)	
Electrodes	Biodegradable conductive: magnesium (Mg), (Boutry <i>et al.</i> , 2018), zinc (Zn), iron (Fe) (Khalid <i>et al.</i> , 2019),	
	Biocompatible conductive: gold (Au) (Chen <i>et al.</i> , 2020; Hosseini <i>et al.</i> , 2020b), silver (Ag) (Amit <i>et al.</i> , 2019), copper (Cu) (Zheng <i>et al.</i> , 2021), Titanium (Ti) (Joseph <i>et al.</i> , 2018), Molybdenum (Curry <i>et al.</i> , 2018)	
	Nanostructures: AgNWs (Koivikko <i>et al.</i> , 2020; Tang <i>et al.</i> , 2021) CuNWs (Song <i>et al.</i> , 2022), AuNPs (Wang <i>et al.</i> , 2018), AgNPs (Lo <i>et al.</i> , 2020)	
Substrate/ Encapsulation	Carbon-based: graphite (Wang <i>et al.</i> , 2020a), carbon nanotubes (CNT) (Wang <i>et al.</i> , 2021; Lu <i>et al.</i> , 2018), carbon black (CB) (Durukan <i>et al.</i> , 2022), activated carbon (AC) (Durukan <i>et al.</i> , 2022), MXene (Chao <i>et al.</i> , 2021)	
	Biodegradable films: PLGA (Khalid <i>et al.</i> , 2019), PCL (Chen <i>et al.</i> , 2020), doped Si (Joseph <i>et al.</i> , 2018; Yogeswaran <i>et al.</i> , 2018), polylactic acid (PLA) (Guo <i>et al.</i> , 2019, Curry <i>et al.</i> , 2018), silk fibroin (SF) (Chao <i>et al.</i> , 2021), PVA (Wang <i>et al.</i> , 2021)	
	Elastomers: Poly (octamethylene maleate (anhydride) citrate (POMaC) (Boutry <i>et al.</i> , 2018), PDMS (Amit <i>et al.</i> , 2019; Wang <i>et al.</i> , 2020b, Pang <i>et al.</i> , 2018; Lu <i>et al.</i> , 2018; Wang <i>et al.</i> , 2018)	
	Biodegradable tapes: Cellulose (Koivikko <i>et al.</i> , 2020)	

fabrication process (Ntagios and Dahiya, 2022; Nikbakht Nasrabadi *et al.*, 2022; Ozioko and Dahiya, 2022; Ozioko *et al.*, 2021b,a; Ozioko *et al.*, 2020). The vital role in capacitive sensing is played by the selection of functional materials as dielectric layer and the conducting electrodes. The capacitance can be described as $C = \epsilon_{\text{air}} \epsilon_r A/d$, where ϵ_{air} is the permittivity of air (8.85×10^{-12} F/m), ϵ_r is the relative permittivity of the dielectric layer, d is the distance between the two electrodes, and A is the covered area of the two electrodes. When external pressure is applied on a parallel plate type capacitive pressure sensors, the thickness of the dielectric layer or the distance between the parallel conducting plates (electrodes) shifts, resulting in the change in the capacitance value, indicating how sensitive is the sensor. In this regard, various degradable functional materials are being explored by the researchers to develop disposable capacitive pressure sensors with excellent performance (Bijender and Kumar, 2022; Dahiya and Valle, 2013).

Recently, an elastomeric material was prepared by incorporating covalent crosslinks and physical hydrogen bonds to prepare a dielectric layer for a capacitive pressure sensor to use for bio-integrated electronics with mechanical and biological properties similar to skin. More specifically, the cross-linked skin-like material poly (sebacoyl diglyceride) (PSeD)-graft-2-ureido-4[1 H]-pyrimidinone unit (PSeD-U) was spin-coated on a silicon wafer mold to form a pyramidal microstructure, as Fig. 1(a) depicts. Sandwiched between two Au-coated PCL films, a capacitive pressure sensor was fabricated with a sensitivity of 0.16 kPa^{-1} and 0.03 kPa^{-1} for the pressure range $< 2 \text{ kPa}$ and $2\text{--}10 \text{ kPa}$, respectively. The biodegradability of the sensor was proved by subjecting the device to 0.1 M Dulbecco's phosphate buffered saline solutions and 2000 U/mL lipase at 37°C (Chen *et al.*, 2020). The results of the cyto- and biocompatibility

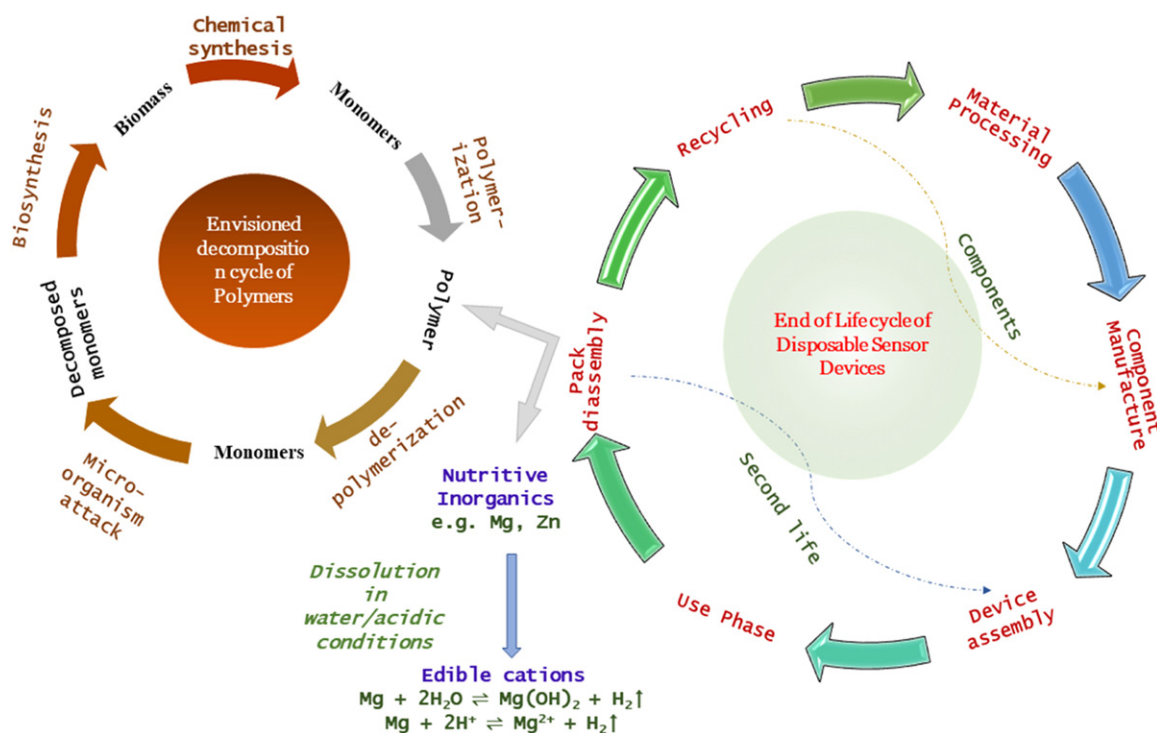


Fig. 1 End of life cycle of disposable sensor devices.

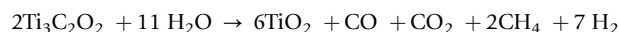
tests of PSeD-U polymers were comparable with the ones of biomaterials such as PLGA. Besides these applications, capacitive pressure sensors have also managed to mark their place in edible electronics. To monitor and treat digestive pressure abnormalities and intestinal motility disorders a piezocapacitive sensing device was fabricated by incorporating gellan gum and gelatin in NaCl or CsCl ionic-covalent entanglement (ICE) conductive hydrogel. The system showed a sensing performance of $0.80 \pm 0.06 \text{ pF kPa}^{-1}$ for the pressures 4–20 kPa which covers the pressure range in the gastrointestinal (GI) tract (0.7–6.3 kPa) (Keller *et al.*, 2017).

When it comes to fabricating sensors for underwater application, designing flexible, lightweight and degradable pressure sensors is a daunting task. In light of this, a capacitive sensor with porous PDMS as dielectric encapsulated in bulk PDMS polymer was fabricated. The sensor exhibited a wide pressure range (0–230 kPa), which is equivalent to the pressure at 23 m below the sea level. Though the degradability of sensor is not demonstrated, but degradability of PDMS is known and hence such work can be extended towards fully degradable sensor, where the electrode could have dissolvable inorganic materials such as Mg (Hosseini *et al.*, 2022).

Resistive

Resistive pressure sensors gained tremendous interest due to their wide range of pressure measurement i.e., 21 kPa to 150 MPa. With a wide pressure range detection along with their short response time, good sensitivity, and ease of fabrication, they are highly desired for practical applications such as, human motion monitoring, medical diagnostics and wearables. The performance of a resistive pressure sensor is evaluated with the change of resistance when an external stimuli is applied. The performance of the sensor is highly connected with the active layer, which is sandwiched between two electrodes and is usually semiconducting composite materials consisting of filaments based on materials such as carbon, as described in Table 2. During loading, a deformity in the active layer leads to resistance variations with the changing distance of the filaments/fillers in materials matrix (Bijender and Kumar, 2022).

Not long ago, a thermally insulated and degradable aerogel was developed as a piezoresistive pressure sensor to monitor different human motion behaviors. Fig. 2(b) illustrates the fabrication process of the aerogel, which includes blending casting of MXene with CCF as the framework material and then freeze-drying for 2 days. The sensor showed a high sensitivity of 61.99 kPa^{-1} (0.4–2.8 kPa), stability for over 1000 cycles and response and recovery time of 300 ms and 150 ms, respectively. After testing the composite aerogel as a pressure sensor, its degradability was evaluated by soaking the sensor in 0.5 M NaOH solution at 18 °C for 40 days. The device collapsed into smaller pieces and eventually degraded, even though some MXene molecules remained in the solution (Zhang *et al.*, 2022a). MXenes are considered as harmless 2D material as according to hypothetical dissolution mechanism of MXenes in water, carbon atoms are converted into carbon dioxide, carbonic acid and some hydrocarbons like methane gas and the overall reaction can be represented as below (Iqbal *et al.*, 2021):



Or

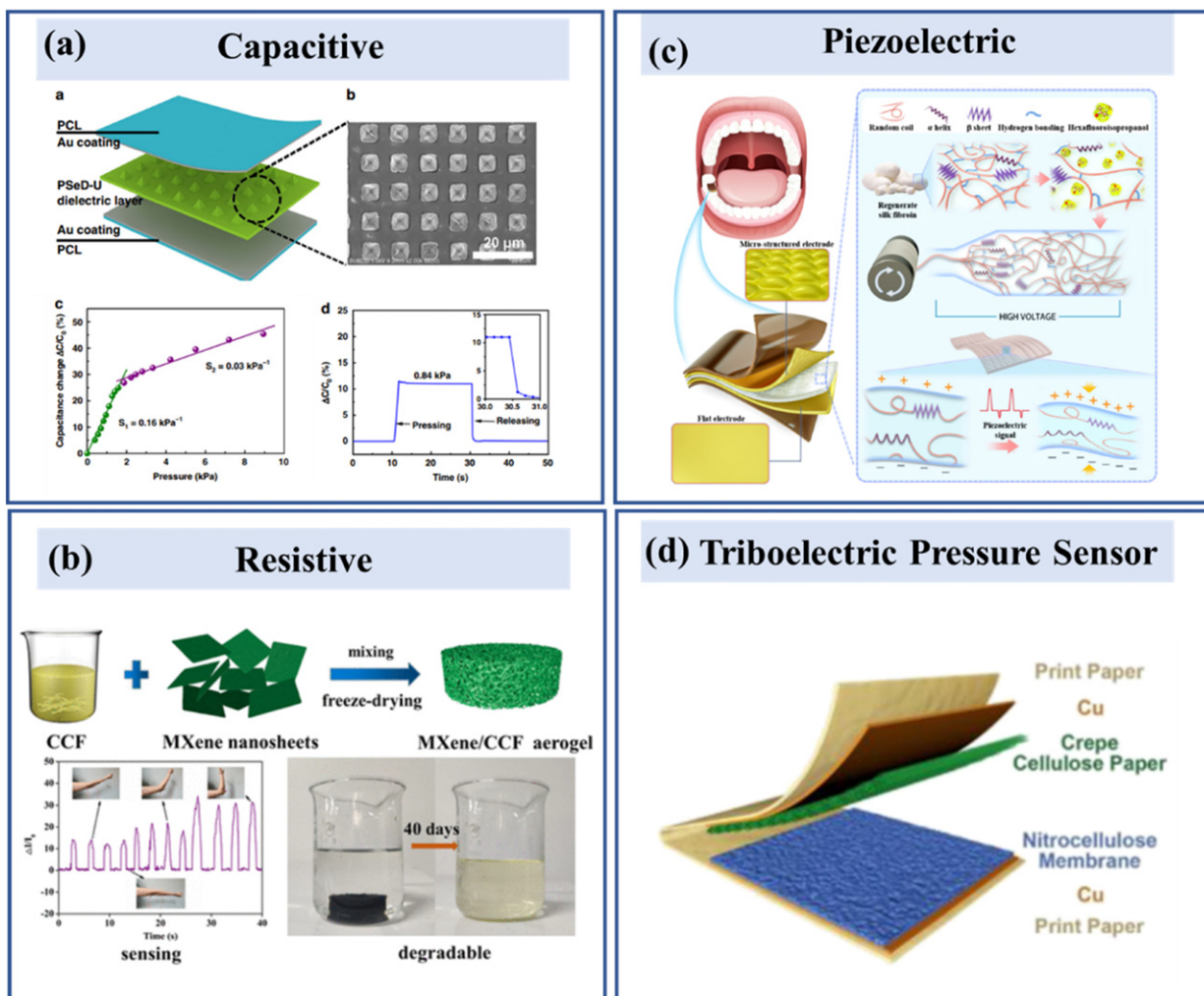


Fig. 2 (a) Schematic illustration and testing of PSeD-U pyramidal microstructured elastomer based capacitive pressure sensor, Preparation and characterization of MXene/CCF aerogels as a resistive sensor, (c) Representation of the fabrication process of the aligned SF electrospun fibers and the potential applications of the piezoelectric pressure sensor, (d) All paper based biodegradable pressure sensor. Reproduced from Chen, S., Sun, L., Zhou, X., *et al.*, 2020. Mechanically and biologically skin-like elastomers for bio-integrated electronics. *Nature Communications* 11, 1107. Zhang, W., Pan, Z., Ma, J., *et al.*, 2022a. Degradable cross-linked collagen fiber/MXene composite aerogels as a high-performing sensitive pressure sensor. *ACS Sustainable Chemistry & Engineering* 10, 1408–1418. Liu, J.-H., Li, W.-D., Jia, J., *et al.*, 2022c. Structure-regenerated silk fibroin with boosted piezoelectricity for disposable and biodegradable oral healthcare device. *Nano Energy* 103, 107787. Chen, S., Jiang, J., Xu, F., Gong, S., 2019a. Crepe cellulose paper and nitrocellulose membrane-based triboelectric nanogenerators for energy harvesting and self-powered human-machine interaction. *Nano Energy* 61, 69–77.



Another biodegradable piezoresistive sensor was developed and used for human motion movement monitoring, virtual reality, and tissue engineering. For the fabrication of the sensor, the elastomeric PGS was mixed with MWCNT and sodium chloride (NaCl) to create porosity. This study proved that the biodegradation of sensors is vital for enhancing their sensitivity. After the fabrication of the sensor, an immersion in a phosphate buffered solution (PBS, pH = 7.4, 37 °C) was followed for its hydrolytic degradation for 8 weeks. The sensitivity was enhanced from $0.12 \pm 0.03 \text{ kPa}^{-1}$ to $8 \pm 0.2 \text{ kPa}^{-1}$, on week 0 and week 8, respectively. The biodegradable resistive pressure sensor exhibited outstanding characteristics since it has small hysteresis, short response time ($\leq 20 \text{ ms}$), and repeatability ($> 200,000$ cycles) (Sencadas *et al.*, 2020).

Piezoelectric

Piezoelectric sensors typically consist of a piezoelectric material which is placed between two conductive plates. Their piezoelectric performance is based on the presence of electric dipoles, which create a separation of electrical charges during external forces. These sensors are dynamic and predictive in nature. In other words, piezoelectric sensors can only be used for dynamic loadings since the piezoelectric materials, which forms the active layer, can generate output voltage signal in response time varying force or pressure

Table 3 Recent advances on disposable pressure sensors.

<i>Capacitive</i>							
<i>Fabrication Technique</i>	<i>Active Layer</i>	<i>Electrodes</i>	<i>Encapsulation/ Substrate</i>	<i>Response/Recovery Time (Jamshidi et al.)</i>	<i>Sensitivity [kPa^{-1}]</i>	<i>Application</i>	<i>References</i>
Electrospinning	PLGA-PCL	Fe-Zn	PLGA thin films	251/170	0.863 ($< 1.86 \text{ kPa}$) 0.062 ($1.86 \text{ kPa} - 4.6 \text{ kPa}$)	Wearable devices	(Khalid <i>et al.</i> , 2019)
Doctor blading	PVA	PVA/CB/AC	–	22/49	0.69 ($< 22 \text{ kPa}$) 0.48 ($24.5\text{--}44 \text{ kPa}$)	Monitoring of physiological signals and body motions	(Durukan <i>et al.</i> , 2022)
Benchtop	PGS	Mg/PLLA	POMaC	–	0.7 ($< 1 \text{ kPa}$) 0.13 ($5\text{--}10 \text{ kPa}$)	Orthopedic application	(Boutry <i>et al.</i> , 2018)
Drop casting	Cross-linked PSeD-U	Patterned/flat Au	PCL	–	0.16 ($< 2 \text{ kPa}$) 0.03 ($2\text{--}10 \text{ kPa}$)	Wearable electronics, biomimetic sensors, medical implants, tissue engineering scaffolds, human–machine interfacing, and soft robotics	(Chen <i>et al.</i> , 2020)
Fused deposition modeling (FDM)	ecoflex	Ag	–	–	0.002115 ($0\text{--}50 \text{ kPa}$)	Soft robotics	(Ntagios <i>et al.</i> , 2020)
Electrode realization with electron beam evaporation	PDMS/ZnO NWs/air gaps	Au/Ti	PDMS	–	0.491 ($0\text{--}10 \text{ kPa}$) 0.047 ($10\text{--}200 \text{ kPa}$)	e-skin	(Kumaresan <i>et al.</i> , 2022)
Spin coating	PDMS/ZnS: Cu phosphor particles	super-flexible transparent wood (STW) film/AgNWs	–	–	1.01 ($< 4 \text{ kPa}$) 0.28 ($5\text{--}80 \text{ kPa}$) 1.15 ($80\text{--}150 \text{ kPa}$)	e-skin	(Tang <i>et al.</i> , 2022)
<i>Resistive</i>							
<i>Fabrication Technique</i>	<i>Active Layer</i>	<i>Electrodes</i>	<i>Encapsulation/Substrate</i>	<i>Response/Recovery Time (Jamshidi et al.)</i>	<i>Sensitivity [kPa^{-1}]</i>	<i>Application</i>	<i>References</i>
Dip coating	MXene- SF	MXene ink	SF membrane	7/16	298.4 ($1.4 - 15.7 \text{ kPa}$) 171.9 ($15.7 - 39.3 \text{ kPa}$)	Smart e-skins, human motion detection, disease diagnosis, and human–machine interaction	(Chao <i>et al.</i> , 2021)
Dip coating	MXene- tissue paper	Ag paste	PLA film	11/25	0.55 ($23\text{--}982 \text{ Pa}$) 3.81 ($982\text{--}10 \text{ kPa}$) 2.52 ($10\text{--}30 \text{ kPa}$)	Personal healthcare monitoring, clinical diagnosis, and next-generation artificial skins	(Guo <i>et al.</i> , 2019)
Dip coating/ thermal reduction technique/ in-suit polymerization	PANI/rGO/Paper	CU foil		70/	143.41 ($0\text{--}0.5 \text{ kPa}$) 0.08 ($0.5\text{--}40 \text{ kPa}$)	Intelligent elements in wearable products	(Zheng <i>et al.</i> , 2021)

(Continued)

Table 3 Continued

<i>Capacitive</i>							
<i>Fabrication Technique</i>	<i>Active Layer</i>	<i>Electrodes</i>	<i>Encapsulation/ Substrate</i>	<i>Response/Recovery Time (Jamshidi et al.)</i>	<i>Sensitivity [kPa^{-1}]</i>	<i>Application</i>	<i>References</i>
Freezing- drying/ chemical vapor deposition	silane-crosslinked and modified graphene aerogel (SGA)	–	–	–	– 67.1 (<1.5 kPa) –8.6 (0.8–1.5 kPa) –14.3 (1.5–2.5 kPa)	Real-time monitoring of subtle actions like the beat of water droplets	(Xiao <i>et al.</i> , 2018)
Freeze- drying	MXene/CCF	–	–	300/150	61.99 (0.4–2.8 kPa)	Human movement monitoring and environmental protection	(Zhang <i>et al.</i> , 2022a)
Freeze casting	MXene/ CNCs	–	–	189/	114.6 (0–10 Pa) 45.5 (0–10 kPa)	wearable devices for detecting biosignals	(Zhuo <i>et al.</i> , 2019)
Freezing- drying	Bacteria cellulose/ caffeic acid- rGO	–	–	120/	13.89 (<2.54 kPa) – 2.71 (2.54–12 kPa)	Health care devices and wearable electronics	(Wei <i>et al.</i> , 2021)
Freezing- drying	MXene/bacterial cellu- lose fibers	–	–	167/121	12.5 (0–10 kPa)	Wearable devices	(Chen <i>et al.</i> , 2019b)
Freezing- drying	Carbonized glucose- dicyandiamide/ CNF	–	–	98/91	10.08 (0–10 kPa)	Wearable devices	(Long <i>et al.</i> , 2021)
Freezing- drying	MXene/rGO	–	–	242/231	4.05 (<1 kPa) 22.56 (1–3.5 kPa)	Measuring pressure distribution, distinguish- ing subtle strain, and monitoring healthy activity	(Ma <i>et al.</i> , 2018)
Mold/hydrolysis	PGS/MWCNT/NaCl	–	–	20/	8 (≤ 8 kPa)	human movement and condition monitoring, recreation, health and wellness, virtual reality, and tissue engineering	(Sencadas <i>et al.</i> , 2020)
Mold/stretching/UVO	micropillar–wrinkle CNT/PDMS	Cu	–	24/	20.9 (0–3 kPa) 2.95 (3–50 kPa) 0.72 (50–100 kPa)	e-skins	(Sun <i>et al.</i> , 2018)
Interfacial polymeriza- tion/ hydrothermal self-assembly	graphene–PANI sponge (GPS)	–	PDMS	50/	0.77 (<6 kPa) 0.05 (30–80 kPa)	Artery wrist pulse, physical signal of human body motions, and wearable electronics	(Huang <i>et al.</i> , 2019)

Piezoelectric

<i>Fabrication Technique</i>	<i>Active Layer</i>	<i>Electrodes</i>	<i>Encapsulation/Substrate</i>	<i>Response time (Jamshidi et al.)</i>	<i>Sensitivity</i>	<i>Application</i>	<i>References</i>
Electrospinning	SF	Au	–	3.4	30.6 mV N ⁻¹ (0–25 N)	Disposable oral medicine devices and in vivo pressure monitoring	(Liu et al., 2022c)
Self-assembly	β -glycine/chitosan	Mg		100	2.82 mV kPa ⁻¹ (5–60 kPa)	Wearable biomedical diagnostics	(Hosseini et al., 2020b)
Heat compression	PLLA	Molybdenum	PLA	–	–	Regenerative medicine, drug delivery, and medical devices	(Curry et al., 2018)
Spin coating	Ultra-smooth silk thin film	Ti	Si/SiO ₂	–	–		(Joseph et al., 2018)
Hot pressing	regenerated silk (RS)/ gold nanorods/ poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)	Carbon tape	silicon rubber	–	–	Tissue engineering	(Bittolo Bon et al., 2021)

Triboelectric

<i>Fabrication Technique</i>	<i>Working mode</i>	Active layers	Electrodes	<i>Encapsulation/ Substrate</i>	<i>Sensitivity</i>	<i>Application</i>	<i>References</i>
Drop casting	Contact separation mode	Positive: Cellulose nanocrystal (CNC)/ methylcellulose (MC) Negative: MC	Graphite	Water soluble adhesive tape	0–2 V	Health care monitoring	(Wang et al., 2022a)
Manual folding	Contact separation mode	Positive: Crepe cellulose paper (CCP) Negative: Nitrocellulose (NCM)	Copper tape	Print paper	196.8 V 31.5 μ A 16.1 W m ⁻² 31.85 V N ⁻¹ (0.5–6 N)	Human–machine interfacing	(Chen et al., 2019a)
Manual synthesis and assembly	Contact Separation mode	Positive: Mg Negative: PLA/CS	Mg	PLA/CS	11 mV mmHg ⁻¹ 0.21 V N ⁻¹	Identify abnormal vascular occlusion events in large animals	(Ouyang et al., 2021)
Molding	Single electrode mode	Negative: PDMS	Carbon fibers (perpendicular directions)	–	0.055 nA kPa ⁻¹ (28.2–41.6 kPa)	e-skin	(Ma et al., 2017)
Electrospinning	Single electrode mode	Negative: PLGA	Ag NWs	PVA substrate	130 mW/m ² 0.011 kPa ⁻¹ ($\leq$ 40 kPa)	e-skin	(Peng et al., 2020)
Manually assembling	Single electrode mode	Positive: Human hand Negative: Starch paper	Metal wire	–		Human perspiration sensing	(Zhu et al., 2018)
Molding	Single electrode mode	Negative: Chitosan (CS)	Au NFs	–	0.012 kPa ⁻¹ (0–70 kPa)	e-skin	(Peng et al., 2022)

and for that reason they are used in applications such as monitoring of human physiological activities and medical diagnostics. This signal can be observed only during the change between on and off modes (Bijender and Kumar, 2022). As for the piezoelectric materials, they are commonly known as materials with the capability to produce electrical charges in response to applied mechanical stresses. Essentially, piezoelectricity is the ability to produce electricity when compressed, twisted, or otherwise subjected to mechanical force/pressure. Bioderived materials with piezoelectric properties, for example amino acids (for instance glycine), collagen, cellulose, and peptide nanotubes, are of great attention over the last few years due to their biocompatibility, renewability, inexpensiveness, and simple and low-temperature processing (Xu *et al.*, 2017; Nikbakht Nasrabadi *et al.*, 2022).

An example of a piezoelectric disposable pressure/force sensor is shown in Fig. 2(c). The sensor comprises of an electrospun mat of aligned SF nanofibers sandwiched between a microstructured Au (bottom) and a flat Au (top) electrode. The sensor has been developed for oral medical diagnosis as well as in vivo pressure sensor for assistive operation (Fig. 2(c)). The device exhibited high sensitivity of 30.6 mV N^{-1} (0–25 N), an ultrafast response time of 3.4 ms and a power density of 5.9 mW/m^2 (Liu *et al.*, 2022c). Similar edible piezoelectric pressure sensors have been fabricated to detect pressure/sounds and mobility in the GI tract (Xu *et al.*, 2017).

Another example of degradable piezoelectric sensor uses self-assembled glycine in chitosan matrix as the active layer, and Mg foil as electrodes (Hosseini *et al.*, 2020b). This self-powered pressure sensor exhibited the sensitivity of 2.82 mV kPa^{-1} (5–60 kPa), which is comparable with non-biodegradable piezoelectric pressure sensors. To evaluate the biodegradability of the sensor, the device was immersed in a phosphate buffer solution (PBS) with pH equal to 7.4. It was noticed that Mg foil got degraded immediately with the immersion of the sensor in the buffer solution while the degradation of the active layer took 2 days. The degradability of such sensor can be controlled by having suitable encapsulation layer. (Table 3).

Tribo-Energy Based Sensing

A material getting charged simply by rubbing against another suitable material has been the very fundamental physics that is typically introduced in the high schools. The very simple experiment of comb rubbed to oily hair attracting bits of paper shows such charge in objects and the like-unlike charge repulsion-attraction. There are number of other examples of charged bodies and their varied principles governing complex devices and their applications. This mechanical rubbing of materials and their charge transfer is the basis of tribo-electricity (Min *et al.*, 2021a,b). A tribo-based energy generator has an active layer and collecting electrodes. First, we should select a pair of materials with opposite triboelectric polarity. Second, we can design various structures to increase the effective contact area between them (Xu *et al.*, 2020). The force with which the materials are separated quantitatively describes the charge generation and transfer. This has been devised to develop different types of sensors including the dynamic pressure sensors (Khandelwal *et al.*, 2021b; Khandelwal and Dahiya, 2022). From the basic mechanism of triboelectricity generation with applied pressure, it is understood that a receiver and a donor is required for generation and effective transfer of electrons. Based on the research until recent years, a triboelectric series of materials has been charted (Khandelwal *et al.*, 2019; Khandelwal *et al.*, 2021a). This also provides a detailed list of biodegradable materials for the active layer (Fig. 3).

When two materials, one from the top of the triboelectric series and another material from the bottom encounter each other, the former loses electrons to the latter and becomes positively charged. This charge transfer increases as the placement of these materials in the triboelectric series increases. Therefore, the charge transfer will be more when a material placed at the top of triboelectric series is rubbed with a material placed at the bottom. Also, TENG performance improves by selection of materials which are far apart in the series. The output voltage of TENGs can be improved by modifying the parameters such as the material composition, surface roughness, surface potential, motion parameters, humidity and temperature effect. The surface and environmental conditions also contribute to the triboelectric series variation. Parameters like charge injection depth, surface charge density, surface capacitance characteristics analysis, interface electrical performance analysis, surface morphology etc. determine the tribo-electrification in materials. Modifying surface texture through morphological changes like pyramids, squares or hemispheres enhances the contact area for more triboelectric effect. In addition, enhancement of triboelectrification can be done by surface functionalization (Khandelwal *et al.*, 2019; Khandelwal *et al.*, 2021a) (Table 4).

Triboelectric principle is applied conventionally to energy generation. However, when applied with sensors for instantaneous mechanical stimuli such as pressure, strain, touch and torsion, the TENGs can help mimic the human mechanoreceptors as self-powered sensors for dynamic pressure sensing. One aspect of integrating sensor with TENGs is using tribo-energy as power source alone and another aspect is using the tribo output itself as sensor output. When used as a pressure sensor, the applied pressure induces more charge and thus a higher output enabling sensing of pressure. Table 3 tabulates this aspect in view of biodegradable materials (Khandelwal and Dahiya, 2022).

Recent research towards obtaining biodegradable alternatives to existing state-of-art pressure sensors is promising in terms of greener sensing solutions. In this context, a paper based TENG sensor using all biodegradable cellulose paper and nitrocellulose membrane with copper electrodes have been proposed. The crepe cellulose paper is found to enhance the tribo-performance by the surface modification due to increasing surface roughness and the corrugated structure, thereby increasing the tribo-active contact area and hence the triboelectric charge density. This work throws light on further human interfacing through piano and force sensitivity of 31.85 V N^{-1} in the range of 0.5–6 N (Chen *et al.*, 2019a). A completely bioresorbable tribo based sensor was proposed using a novel approach and sensor performance was monitored by in-vivo implantation inside the skin. The study was carried out in dogs and the performance degradation was observed 4–5 days after implantation. The biodegradation study was performed at constant temperature in PBS solution. The tribo materials and electrode were observed to undergo chain splitting reaction during hydrolysis and degradation in the amorphous region of PLA/CS. They break down into polymer fragments that are absorbed in vivo such as lactic acid, carbon dioxide, water so on. The mass

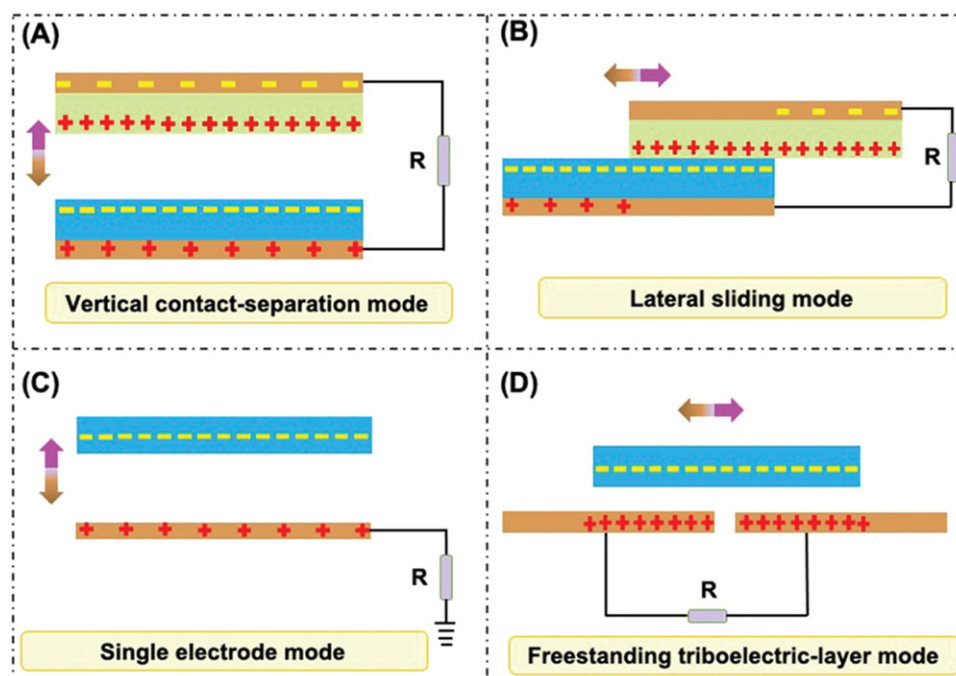


Fig. 3 Working modes of triboelectric generators. (A) Vertical contact-separation mode, (B) lateral sliding mode, (C) single-electrode mode, and (D) freestanding triboelectric layer mode. Reproduced from Khandelwal, G., Dahiya, R., 2022. Self-powered active sensing based on triboelectric generators. *Advanced Materials* 34, 2200724.

Table 4 Evaluation of different working modes of TENG devices

Sl. No.	Mode of operation	Pros	Cons
1	Vertical Contact – Separation (CS)	Stable and high performance, easy to design, simple structure	Discontinuous AC output, Issues of wear and tear
2	Lateral Sliding (LS)	High triboelectric effect	low current output,
3	Single Electrode (SE)	Simple fabrication and design, has one free layer	effect of temperature and humidity, SE mode requires ground
4	Freestanding Triboelectric – layer (FT)	Highest performance in CS design, one freely moving layer	FT layer mode has complex fabrication procedure and structure

reduction over a period of time was monitored and found to drop by 0.78% after 3 days. The magnesium electrode layers inside device degraded after 8 days and the complete device degraded in vitro after 63–84 days. The device output dropped from initial 4.2–1 V after 4 days and once the encapsulation layer of PLA/CS was broken down. The device stopped working due to liquid penetration and resulting damage. As the device performance is monitored in vivo, the blood pressure leads to the contact separation based charge induction. Typically, it is synchronised with the diastole and systole blood pressure phases. In the systolic phase, the sensor is compressed by the blood vessel leading to an increased output voltage; while in the diastole phase, the pressure on sensor is released leading to withdrawal of accumulated charges and lowering the output voltage (Ouyang *et al.*, 2021).

Conclusion

Considerable advancement has been made by the scientific community in terms of exploring biodegradable materials for potential pressure sensor applications. Modifying materials by tuning their structure with ligand functionalization or incorporating polar functional groups can enhance their physical as well as biological characteristics. However, biodegradable sensors require a complete metabolization of each component of the sensor. Understanding degradation cycle of materials under more natural conditions apart from artificial environment needs considerable combined efforts from science and engineering. Besides, reshaping materials, ecodesign of the sensor devices can be revolutionary in its own way as it considers the safe recycling aspect of various components. Thus, a new perspective for circular electronics is needed which not only exploits the use of degradable and unarmful novel materials as potential candidate for sensor components but also considers the eco-design of the device.

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ZnO Nanowire Based Flexible Transient Ultraviolet Photodetectors

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Abstract

An ultraviolet (UV) light sensitive electronic skin (e-skin) or sensor patch could lend new abilities to robots and humans by allowing them to operate in suitable light-sensitive environments or record the safe levels of UV exposure to prevent ailments such as skin cancer. Development of these sensors in flexible form factors could also enable interesting wearable system applications and potentially revolutionise the digital healthcare sector through them. This chapter discusses the recent advances in the development of ZnO nanowires (NWs) based high-performance UV photodetectors with focus on devices fabricated on flexible and degradable substrates. The chapter also surveys the resource-efficient fabrication routes adopted to develop such flexible and transient UV photodetectors.

Nomenclature

PDMS Polydimethylsiloxane

UV Ultraviolet

NW Nanowire

E-skin Electronic skin

PECVD Plasma-enhanced chemical vapour deposition

DIW Direct Ink Write

1D, 2D, 3D One dimensional, Two dimensional, Three dimensional

Biocompatibility The ability of a material to perform with an appropriate host response in a specific situation

Transient Electronics New class of electronic devices that can operate in certain conditions for a prescribed time and then degrade either naturally or in a certain medium.

Electronic skin The multisensory interface that mimics the properties of human skin such as receptors, stretchability, self-healing, dexterity, efficient computing etc.

Soft sensors Sensors that are mechanically flexible and/or stretchable

Key Points

- A concept of ultraviolet (UV) light sensitive electronic skin is presented.
- A resource-efficient printed electronics route to develop UV photodetectors is discussed.
- Contact printing of ZnO nanowires offer potential to realise flexible and transient UV photodetectors.
- Applications of flexible and transient UV photodetectors in healthcare are discussed.

Introduction

Electronic skin (e-skin), which mimics the morphology and functionalities of the biological skin, holds great promise for the development of wide range of applications including health monitoring, rehabilitation, robotics, environment monitoring, Internet of Things etc. (Paul *et al.*, 2022; Neto *et al.*, 2022; Ma *et al.*, 2022b; Kumaresan *et al.*, 2022b, a; Dahiya *et al.*, 2019b,a; Dahiya, 2019). The capability of e-skin could be augmented with new types of sensors, which are not normally present in the biological skin. For example, ultraviolet (UV) detectors could be integrated on flexible substrates to develop e-skin patches for wearable dosimetry applications (Zumeit *et al.*, 2022; Núñez *et al.*, 2018; García Núñez *et al.*, 2018a). Controlled UV light exposure to biological skin (hereafter ‘skin’ only) has health benefits including enabling the production of Vitamin D, which is needed for stronger bones and muscles (Chen *et al.*, 2015; Kalajian *et al.*, 2017). However, its excessive exposure could lead to adverse health conditions such as skin cancer (Boyes and Stanisstreet, 1998), damaging the DNA of eyes, accelerate skin aging process etc. (Ivanov *et al.*, 2018; Mohania *et al.*, 2017; Park *et al.*, 2019). Also, the excessive exposure to UV radiations could adversely impact other areas, for example, agricultural production (Chen *et al.*, 2015). Inspired by the skin morphology and functionality (Fig. 1(a)), electronic-skin (e-skin) technology is gaining attention for emerging applications in which electronics is required with novel form factors including flexibility and stretchability (Zumeit *et al.*, 2022; Neto *et al.*, 2022; Murali *et al.*, 2022; Liu *et al.*, 2022b,a; Sachyani Keneth *et al.*, 2021; Dahiya *et al.*, 2021; Soni and Dahiya, 2020). An ultraviolet light sensitive e-skin conformal enough to cover

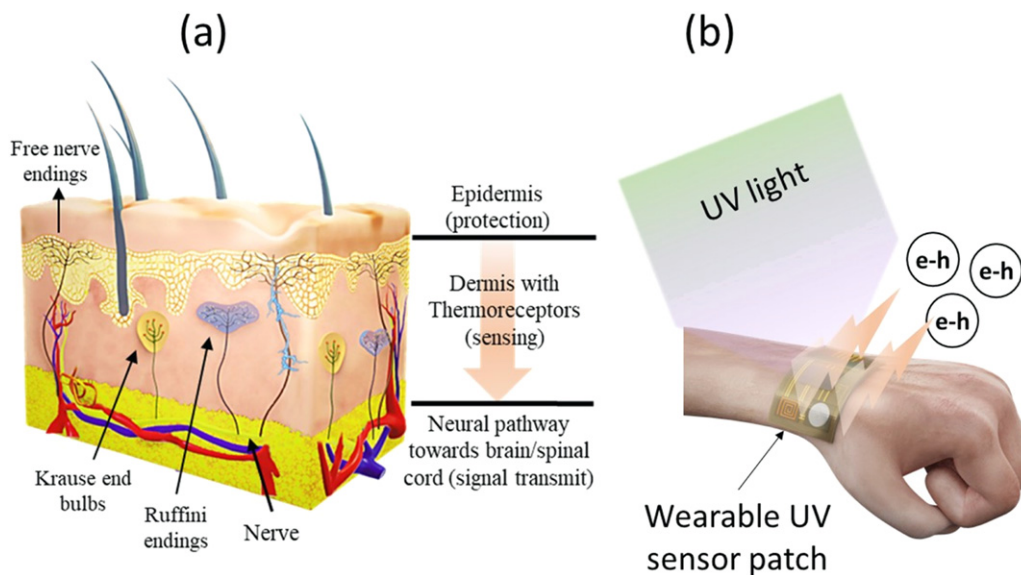


Fig. 1 (a) Schematic representation of skin model with various sensory receptors inside the soft tissue. (b) E-skin wearable patch with mechanically soft sensors to detect UV light. Reprinted from Neto, J., Chirila, R., Dahiya, A.S., *et al.*, 2022. Skin-inspired thermoreceptors-based electronic skin for biomimicking thermal pain reflexes 9 (27), *Advanced Science* 2201525.

nonplanar surfaces such as skin, and plants surfaces can help advance the application domain to monitoring of UV radiation under diverse environmental conditions (Fig. 1 (b)). Linking such an e-skin to a communication network could also allow patient-doctor communications periodically or in real-time for digital healthcare (Dahiya *et al.*, 2020b). Furthermore, extending the abilities of the e-skin to detect wide wavelength of light (UV to infra-red range) could endow new features to robots used for manufacturing in light-sensitive environments (Zumeit *et al.*, 2022).

Most of the available commercial wearable/portable UV sensors are made of rigid materials and developed using conventional microfabrication processes such as metal lift-off, etching, photolithography etc. Enormous efforts have been made to achieve flexible and stretchable UV PDs to go beyond the existing silicon-based rigid electronics (Meng *et al.*, 2020; Kim *et al.*, 2020a; Lien *et al.*, 2018; Han *et al.*, 2016; Trung and Lee, 2017; Kumaresan *et al.*, 2021). Unlike conventional electronic devices, materials for soft and wearable sensors require unique properties such as flexibility, stretchability, and biocompatibility (Zumeit *et al.*, 2022; Ozioko and Dahiya, 2022; Ntagios and Dahiya, 2022; Nikbakhtnasrabadi *et al.*, 2022; Neto *et al.*, 2022; Liu *et al.*, 2022a; Beniwal *et al.*, 2022; Kumaresan *et al.*, 2021; Dahiya *et al.*, 2021). Significant progress has been made for the development of portable and wearable UV sensors, with novel form factors. As active UV sensing materials, nanostructured semiconducting materials have been extensively studied for flexible electronics (Dahiya *et al.*, 2022a; Shakthivel *et al.*, 2019; Núñez *et al.*, 2018). Because of their low-dimensionality, they exhibit high mechanical flexibility, large surface-to-volume ratio as well as efficient charge transport. Among various nanomaterials, zinc oxide (ZnO) nanostructures particularly stand out because of their low toxicity, biocompatibility, biodegradability as well as simple, economical and environmentally friendly synthesis approaches (Liu *et al.*, 2022b; Dahiya *et al.*, 2022a; Dahiya *et al.*, 2018b,a; Dahiya *et al.*, 2017; Dahiya *et al.*, 2016; Barbagiovanni *et al.*, 2016; Opoku *et al.*, 2015). Furthermore, ZnO nanostructures have shown advantages in UV sensing applications due to their direct wide band gap (~ 3.34 eV), large exciton binding energy (60 meV), high UV absorption coefficient, and therefore high UV sensitivity and selectivity. Accordingly, ZnO nanostructures have been widely investigated for UV sensing with different device prototypes such as p-n junction (Wang *et al.*, 2016), Schottky junction (Zhang *et al.*, 2017), etc and with novel form factors including stretchable (Kumaresan *et al.*, 2021) and biodegradable (Dahiya *et al.*, 2022a).

To date, most of the UV photodetectors have been fabricated employing conventional, subtractive processes involving photolithography, chemical etching, etc (Chakraborty *et al.*, 2022). Despite the maturity and compatibility with large-scale fabrication, an excessive chemical waste is generated through these processes, in addition to a high manufacturing cost. Considering the environmental impact, an alternative manufacturing route with high resource-efficiency is required. From this perspective, printed electronics have been explored to open new avenues towards an energy efficient and resource efficient fabrication approach (Neto *et al.*, 2022; Liu *et al.*, 2022b; Dahiya *et al.*, 2022b,a; Shakthivel *et al.*, 2021; Kim *et al.*, 2020b; Dahiya *et al.*, 2020a; Khan *et al.*, 2015). This chapter presents the resource efficient fabrication route to develop UV photodetectors on flexible and biodegradable substrates using ZnO nanowires (NWs).

UV Sensing Mechanism for ZnO NW-Based Photodetectors

In literature, a variety of device prototypes for sensing UV light using ZnO NWs are reported. The sensing mechanism is specific to their unique device structure. In this section, first, the sensing mechanism common to all device prototypes of ZnO NW-based UV

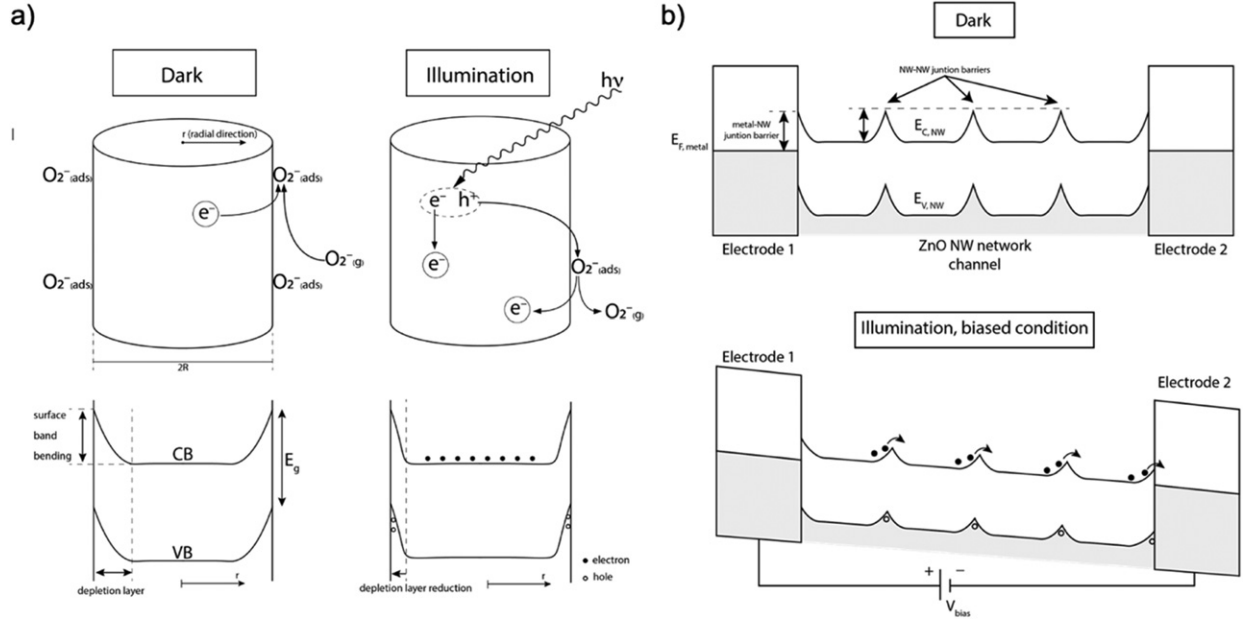


Fig. 2 (a) (Above) schematic illustration of the processes occurring in the ZnO NW in dark and UV illumination condition and, (below) the respective NW band structure; (b) charge transport mechanism in a ZnO NW network-based photodetector.

sensors is presented. Then, the sensing mechanism specific to different devices such as having a Schottky barrier at the metal-NW (semiconductor) interface (Dahiya *et al.*, 2022a) and devices with many potential barriers due to multiple NW-NW interfaces (Kumaresan *et al.*, 2021) are discussed.

The photoconductivity mechanism of a single ZnO NW based device is illustrated in Fig. 2 (a). The oxygen species available in ambient conditions are chemisorbed on the surface of a ZnO NW and capture the free electrons from the NW. The process results in the formation of a depletion region extending in the radial direction from the NW surface, and thus the energy bands bend in an upward direction (Kushwaha and Aslam, 2012). The bulk ZnO has an energy bandgap of about 3.34 eV (Barbagiovanni *et al.*, 2016; Dahiya *et al.*, 2014), which corresponds to a photon wavelength of ~ 370 nm (in the UVA range). So, when a photon with the wavelength ≤ 365 nm is illuminated on the ZnO NW based devices, the photon gets absorbed by the NW and an electron-hole ($e-h$) pair is generated. Because of the electric field developed in the depletion region, the photogenerated $e-h$ pair separates. The free electron directly contributes to the device's current, while the hole migrates to the ZnO NW surface, where it reacts with one of the adsorbed oxygen anions and results in the desorption as a gaseous oxygen molecule and the release of a captured electron. This further enhances the device conductivity. Thus, for one photon absorbed, two electrons are generated. Further, when a UV light with increasing intensity is illuminated on the NW, more and more photons are absorbed by the NW and, so, a larger concentration of free electrons becomes available for conduction, decreasing the width of the surface depletion region and progressively reducing the surface band bending. The increase of the device conductivity with UV light intensity is sublinear due to saturation of oxygen desorption sites and an increase of hole de-trapping dynamics from these sites with increasing carrier density (Mallampati *et al.*, 2015).

When, in ambient conditions, the UV illumination is turned off, recombination of $e-h$ pairs occurs. Therefore, on the NW surface, the equilibrium shifts again towards the absorption of the available oxygen species, which trap again free electrons. Thus, the surface band bending, and the initial depletion layer appears again, leading to a decrease in the device conductivity. To better frame the importance of oxygen in the sensing mechanism, it is noteworthy to mention that the ZnO NWs present a long-term persistence of photoconductivity (Bao *et al.*, 2011) when oxygen species are not available in the environment (as an example, in vacuum).

The simplest of a NW-based photodetector structure requires two metal electrodes at each end of the NW. The length of the NW between two electrodes (device channel) defines the sensing area of the photodetector. Therefore, to address the overall photo response mechanism, it is critical to take the metal-NW (semiconductor) junction into account while defining the sensing mechanism. It is well-established that a Schottky-type metal-semiconductor (MS) contact forms when a metal with the work function ϕ_m larger than the semiconductor's electron affinity χ is deposited. The energy barrier of such a Schottky contact is generally defined by $(\phi_m - \chi)$ (Sze and Ng, 2006). Under ambient conditions, the ZnO NW surface is negatively charged. The negative charges contribute to an increase of the potential energy barrier level at the MS contact and thus, further impede the current flow. When NWs are illuminated by UV light, the decrease of negative surface charges leads to a decrease of barrier height, which in turn leads to an exponential increase of the device current. Moreover, a NW-based photodetector with the Schottky contacts having higher potential barrier is expected to display faster photo response (Dahiya *et al.*, 2022a).

Many ZnO NW-based UV sensors are fabricated with NW networks in the channel area. The NW network is obtained by various techniques such as drop casting (Kumaresan *et al.*, 2021) or spray coating (Yalagala *et al.*, 2023) of a NW dispersion. In this case, the free electrons flowing through the sensing channel meet multiple NW-NW interfaces. Because of the nanostructure's surface band bending, each interface represents an additional resistance to the current flow (Fig. 2 (b)). When the photodetector is illuminated by UV light, the increase of carrier concentration leads to a decrease of the depletion layer width and to a decrease of the energy barrier height for each NW-NW junction. Therefore, in the case of NW mesh-based channels, this additional mechanism further contributes to the overall decrease of resistance when the device is turned from dark to UV illuminated condition. These mechanisms are particularly important when accounting for the performance of flexible sensors, as the number and nature of the NW-NW junctions may change in the different bending states and could possibly lead to a different device performance.

Key Performance Parameters

Multiple parameters and figures of merit (FoM) are used to provide an exhaustive representation of the photodetector's performances. In order to characterise the signal-to-noise ratio, the on-off current ratio (also referred to as light-to-dark current ratio) $I_{\text{light}}/I_{\text{dark}}$ is used, where I_{light} and I_{dark} represent the current flowing through the device in dark and illumination conditions, respectively. The photogenerated current is defined by:

$$I_{\text{photo}} = I_{\text{light}} - I_{\text{dark}}$$

The photogenerated current obviously depends on the power of the incident light and, thus, on the light intensity P_{in} and on the area of the sensing area of the photodetector S . To account for this, the responsivity is defined by (Dahiya *et al.*, 2022a):

$$R = \frac{I_{\text{photo}}}{P_{\text{in}} \times S}$$

Another fundamental photodetector FoM is the specific detectivity, which is closely related to the noise current and device responsivity (Dahiya *et al.*, 2022a):

$$D^* = \frac{R\sqrt{S}}{\sqrt{2} \cdot e \cdot I_{\text{dark}}}$$

The equivalent signal-to-noise ratio from a quantum perspective is the external quantum efficiency EQE , which is the ratio of photogenerated electron-hole pairs per incident photon. For a given photon wavelength, it can be calculated by (Yalagala *et al.*, 2023):

$$EQE(\%) = R \times \frac{hc}{\lambda_{\text{incident}}} \times 100(\%)$$

In terms of device temporal response, the characteristic times the device takes to switch from dark to illumination conditions and vice versa are defined as the *response time* and *recovery time*, respectively. The exact definition of these characteristic times is arbitrary. According to one of the well-established and accepted conventions, the response time is defined as the time interval in which I_{light} passes from 10% to 90% of the saturated response and vice versa for the recovery time (Yalagala *et al.*, 2023).

Resource-Efficient Fabrication by Printing

Conventionally the sensors and other electronic devices are fabricated by employing standard micro/nano fabrication process steps, which include photolithography, etching, etc. However, these steps have the following major drawbacks (Mullen and Morris, 2021): (i) they generate large amounts of electronic waste (e-waste) both during the fabrication and product's end-of-life, (ii) the fabrication plant (commonly called a fab) requires a huge investment and resources such as water and energy, and (iii) most of these steps are not compatible with flexible and transient substrates. Printed electronics offers attractive solutions to address these challenges and thus, has gained significant attention in recent years. This is owing to excellent traits including efficient use of materials as an additive manufacturing route, negligible toxic waste generation during printing, design flexibility (maskless designs), low fabrication cost, and possibility to realise devices on diverse substrates including plastics and biodegradable substrates. The following section discusses how to print high grade ZnO NW based electronic layers and metal interconnects.

Development of Electronic Layers Based on ZnO NWs

Significant progress has been made in the last two decades to print/assemble ZnO NWs using both dry and wet methods (Fig. 3) (Yalagala *et al.*, 2023; Neto *et al.*, 2022; Liu *et al.*, 2022b; Dahiya *et al.*, 2022a; Gupta *et al.*, 2018; García Núñez *et al.*, 2018b; Zumeit *et al.*, 2022; Zumeit *et al.*, 2021). These techniques aim to achieve high transfer yield, precise placement, directional alignment, high density, uniform interspacing, monolayer control, and ability to transfer NWs over wide range of flexible and transient substrates. Among these printing techniques, contact printing is a promising dry transfer method, wherein directional physical

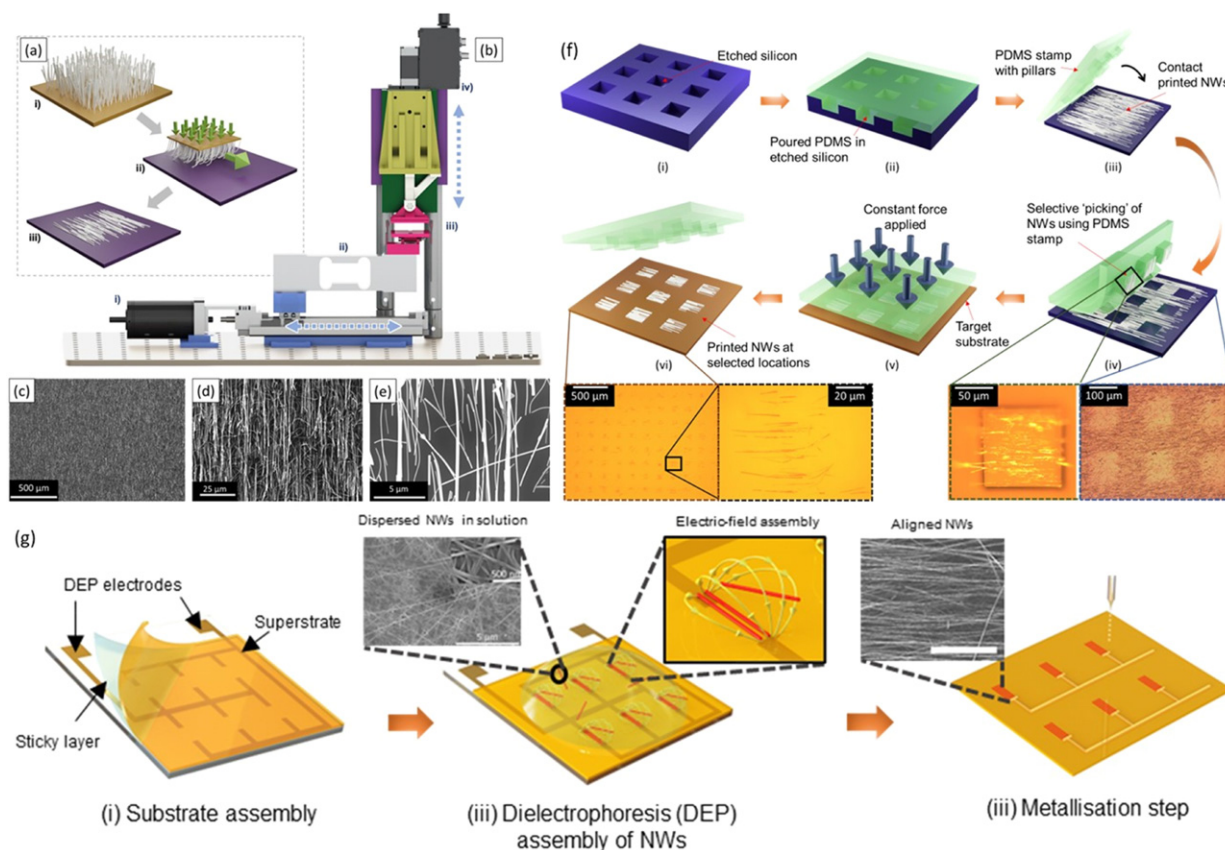


Fig. 3 Nanowire based electronic layer assembly techniques. (a) Schematic showing the contact printing process steps: (i) donor with vertically grown NWs, (ii) Controlled vertical pressure and sliding of donor over receiver substrate, and (iii) printed and aligned NW layer. (b) Schematic of the custom-built system: (i) horizontal stage, (ii) load cell, (iii) self-aligning platforms, and (iv) vertical stage. (c-e) SEM images of the contact printed NWs at different magnifications. (f) In-tandem contact transfer printing of NWs: Schematic illustration of various steps involved in selective printing of ZnO NWs: (i) fabrication of master silicon template using photolithography and etching, (ii) fabrication of PDMS stamp using master template, (iii) placement of PDMS stamp with pillar structures onto contact printed NWs, (iv) selective transfer of NWs onto the PDMS stamp (inset shows the optical images of PDMS stamp with transferred NWs on pillars (left) and selectively removed NWs from contact printed NWs (right)), (v) PDMS stamp with NWs in conformal contact with the target device substrate and (vi) selectively printed NWs over target device substrate (inset shows the optical images of the printed NWs at different magnification). (g) Dielectrophoresis (DEP) NW assembly process: (i) superstrate (substrate on which NWs are aligned) attached over DEP electrodes using thin double side tape. (ii) DEP process for precise and oriented assembly of NWs; inset (left) shows SEM image of the entangled (non-aligned) NWs and inset (right) shows electric field lines to trap NWs; (iii) printing to define metal electrodes and interconnects; inset shows the magnified SEM image of the aligned NWs. Reprinted with permission from Dahiya, A.S., Christou, A., Neto, J., *et al.*, 2022a. In tandem contact-transfer printing for high-performance transient electronics, *Advanced Electronic Materials* 8, 2200170. Neto, J., Chirila, R., Dahiya, A.S., *et al.*, 2022. Skin-inspired thermoreceptors-based electronic skin for biomimicking thermal pain reflexes. *Advanced Science* 9 (27), 2201525.

sliding of NW substrate (which is a donor substrate) over a receiver (flexible or transient) substrate to print horizontally aligned NWs uniformly (Fig. 3 (a-e)) (Christou *et al.*, 2021; García Núñez *et al.*, 2018a). Contact printing offers advantages such as: (i) highly directional alignment of nanostructures, which is needed for high-device performance, (ii) single-step process, (iii) cost-effective, and (iv) avoids contamination to NW surface as it is a dry printing method. This technique yields high density of aligned NWs uniformly over entire substrate area (Fig. 3 (a-e)). Apart from ZnO NWs, the approach has been used to print other inorganic materials as well, including Si, carbon nanotubes, Si/Ge (core-shell), etc. As the process avoids the use of toxic chemicals and lithography steps, it is largely a green process. However, the printing approach has technological challenges such as the NWs are printed uniformly over an entire substrate area. Because of this, it is challenging to print different functional materials on the same substrate, thus avoiding heterointegration. Further, the resulting device architecture could lead to crosstalk among neighbouring sensing structures. Printing NWs at selective locations could help in addressing these challenges (Fan *et al.*, 2008a). Contact printing has been used to directly print the NWs at selected location (Fan *et al.*, 2008b) but the lithography and surface treatment needed each time to define the NW locations which will make it cumbersome for large scale integration and contaminations by surface treatment step could influence the electrical properties of NWs. In this regard, a versatile in-tandem contact-transfer printing is advantageous (Dahiya *et al.*, 2022a) (Fig. 3 (f)). The approach is schematically shown in Fig. 3 (f). Not only does the in-

tandem approach address the challenges related to contact printing but also those of transfer printing method which suffers from limitations such as choice of active material (limited by the availability of a bulk-wafer) and repeated use of photolithography to define the nanostructures. The in-tandem approach is advantageous to print electronic layers, since: (i) it is suitable on wide range of materials systems, (ii) it allows printing at selective locations and (iii) it is resource-efficient and eco-friendly, as it avoids the use of repeated photolithographic steps. The authors demonstrated the in-tandem approach capability to print ZnO NWs at selective locations and then processed these electronic layers to fabricate UV photodetectors on flexible and transient substrates. To achieve this, first, contact printing was used to print highly laterally aligned ZnO NWs on an intermediate rigid substrate to obtain uniform electronic layers. Then, transfer printing is employed to collect NWs from the printed layers and selectively print them on the final substrate.

The solution-processable NWs assembly methods including dielectrophoresis (DEP), Langmuir – Blodgett (LB), spray coating etc. have also been used to print NW electronic layers. These methods have advantages simplicity, cost-effectiveness, and scalability. Particularly, DEP offers precise positioning of NWs with a high degree of orientation at a much faster speed, which gives potential for high-throughput process (Fig. 3 (g)). In a standard DEP process, a suitable voltage (AC or DC) is applied across pre-defined microelectrodes to induce a non-uniform electric field which leads to the generation of a DEP force across the nanostructures to eventually align them (Neto *et al.*, 2022; Liu *et al.*, 2006). DEP is compatible for site specificity, single or dense NW alignment, large areal coverage and layer by layer assembly. However, DEP requires a uniform dispersion of NWs, which, thus, require NW surface modification. This could contaminate the NW surface and lead to poor device performance.

Defining Metal Contacts, Interconnects, and Packaging

Considering the environmental impact of conventional microfabrication processes to define metal electrodes and interconnects, printing could also be utilised as an energy and resource efficient fabrication approach (Khan *et al.*, 2015). This could be achieved using a variety of commercially available contact and non-contact printers. The prominent non-contact printing techniques include slot-die coating, screen, and jet-based printing (such as super inkjet, inkjet, and aerosol printing), whereas the contact-based printing comprise of gravure, gravure-offset, flexographic, transfer, and nanoimprinting. The details on printing resolutions, mechanism, advantages, and disadvantages of available printing techniques can be found elsewhere (Khan *et al.*, 2015). There have been several research works focused on printed sensors, transistors and circuits using contact and non-contact printers (Neto *et al.*, 2022; Ma *et al.*, 2022a; Dahiya *et al.*, 2022a; Migliorini *et al.*, 2021; Liang *et al.*, 2021; Sun *et al.*, 2020; Khan *et al.*, 2015). However, considering the poor printing resolution (30–100 μm) of most of the available printers such as screen and inkjet printer, it is difficult to achieve printed sensors based on ZnO NWs whose length typically varies between 10 and 30 μm . Further, issues such as coffee ring effects, line bulges and discontinuous printing while using inkjet technique often limit its application wherein fine patterning is required. Recently, techniques offering a higher resolution (1–10 μm), as an example extrusion-based Direct Ink Write (DIW) and electrohydrodynamic (EHD) based jet printing have arisen (Neto *et al.*, 2022; Ma *et al.*, 2022a; Dahiya *et al.*, 2022a). Extrusion based DIW printers generally print high viscosity ink/paste whereas EHD-based jet printing requires low-viscosity inks. Therefore, the advantages of adopting these drop-on-demand printing techniques to realise all-printed ZnO NW photodetectors are (i) capability for high-resolution printing (1–10 μm); (ii) substrate independent patterning; (iii) simplicity and low fabrication cost process (single-step additive printing); (iv) maskless (digital) metal patterning; and (v) environmentally benign process (no chemical wastage). In the authors' opinion, both (EHD-based and DIW) are commercially viable approaches that could maintain low fabrication cost, and reduced material and energy wastage to drive down the price and allow market accessibility for the fabrication of ZnO NW based printed UV sensors.

Design Prototypes for ZnO NWs Based UV Photodetectors

The printed ZnO NW-based electronic layers have been employed to fabricate different prototypes of flexible (Fig. 4) and transient (Fig. 5) UV photodetectors. In this section we describe some prominent examples of the reported prototypes.

Flexible UV Photodetectors Based on Printed ZnO NWs

A uniformly printed electronic layer is needed to achieve low device-to-device response variability. Towards this, a semi-automated contact printing system that allows control over contact force, sliding speed and sliding stroke, was used to print a uniform ZnO NW layer over an entire polyimide substrate (Fig. 3 (b)) (Christou *et al.*, 2021). The fabrication of metal contacts was realised using conventional photolithography and metal lift-off steps. In this device prototype, each photodetector has multiple NWs in the sensing channel, wherein each NW constitutes a parallel channel for current conduction. The device's performances are strongly dependent on the number of NWs in the channel and their dimensions. Using this approach, a 5×5 array of photodetectors, having ~ 40 NWs in the channel area, was realised (Fig. 4 (a)). The two-terminal current-voltage (I-V) characteristics showed a linear dependence, indicating ohmic contact between the NWs and the electrodes. The 25 devices in the array showed uniformity in their time-resolved photoresponse curves (Fig. 4 (b)). Indeed, each device was characterised applying a bias voltage of 1 V, while

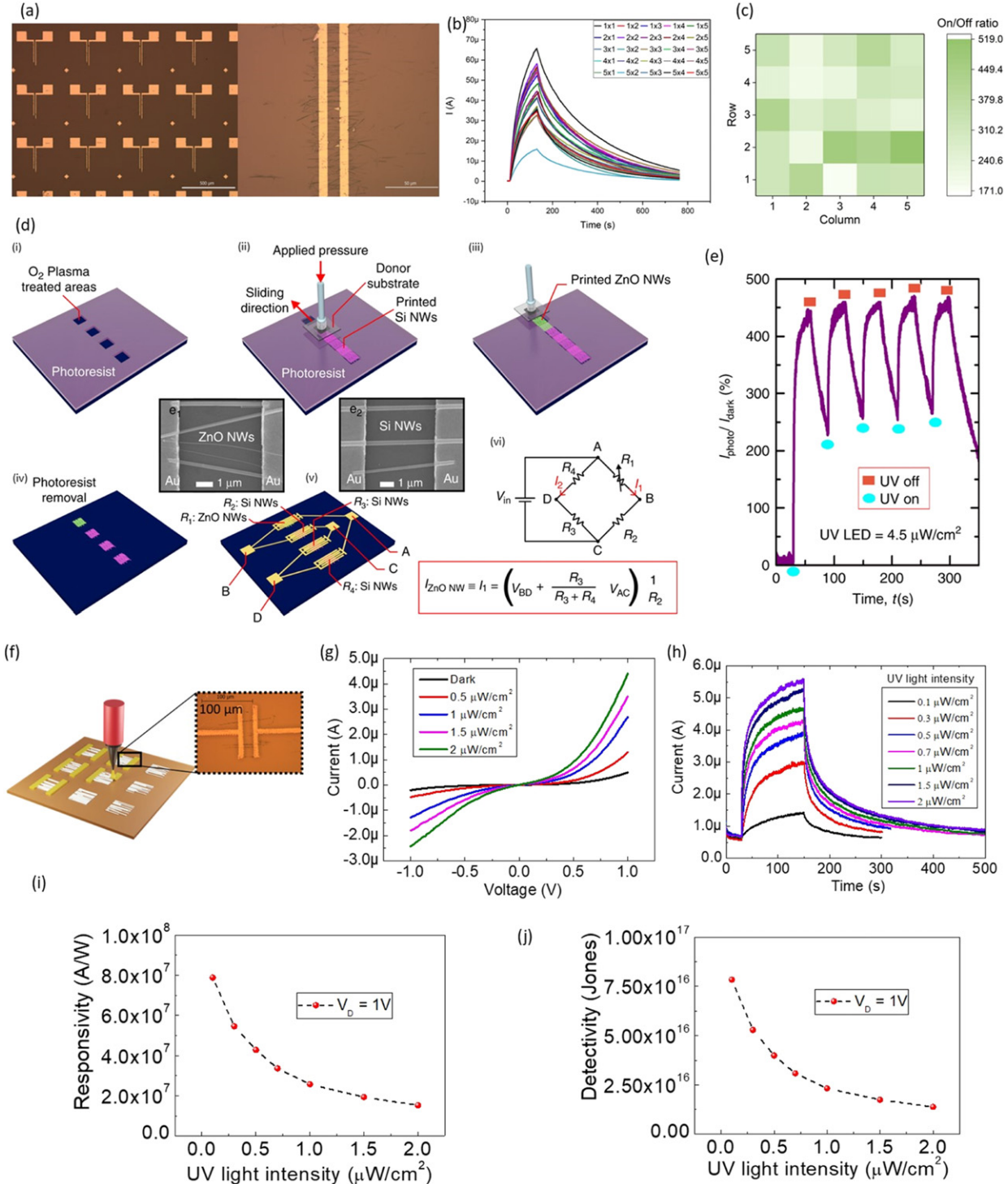


Fig. 4 Flexible photodetectors using ZnO NWs electronics layers: (a) optical microscope images of (i) the 5×5 array of contact printed NW photodetectors and (ii) detail of the channel region; (b) time-resolved photoresponse curves from 25 devices, (c) heatmap showing the level of uniformity of on-off current ratio of the devices in the 5×5 array. (d) Schematic illustration of the fabrication steps for ZnO and Si NW-based photodetectors in Wheatstone bridge configuration: (i) a definition of 20 mm^2 areas on a S1818 photoresist layer by photolithography, followed by an O_2 plasma treatment (100 Watt and 0.3 mbar for 1 min); contact-printing of (ii) Si and (iii) ZnO NWs; (iv) removal of the photoresist in warm acetone (50°C for 2 min); (v) definition of $\text{Ti}(4 \text{ nm})/\text{Au}(200 \text{ nm})$ interdigitated electrodes by photolithography and lift-off, where (e1) and (e2) show SEM images of printed ZnO and Si NWs, respectively, bridging a pair of Ti/Au electrodes with a $5 \mu\text{m}$ gap. (vi) WB equivalent circuit and the expression determining the electric current flowing through ZnO NWs ($I_{\text{ZnO NW}}$). (e) Multi-cycles measured over time and using a UV LED power density of $4.5 \mu\text{W}/\text{cm}^2$ and a V_{in} of 0.05 V , keeping a distance between UV LED and the PD surface of 5 cm . (f-j) In-tandem contact transfer printing technique to realise printed photodetectors and characterisations: (f) schematic of EHD printing on selectively transferred ZnO NWs, (g) I-V characteristics under dark and UV light at different intensities, (h) response to UV light with different intensities from 0.1 to $2 \mu\text{W}/\text{cm}^2$, (i) responsivity, and (j) specific detectivity curve at different UV light intensities. Reprinted from Christou, A., Liu, F., Dahiya, R., 2021. Development of a highly controlled system for large-area, directional printing of quasi-1D nanomaterials. *Microsystems & Nanoengineering* 7. García Núñez, C., Liu, F., Navaraj, W.T., *et al.*, 2018a. Heterogeneous integration of contact-printed semiconductor nanowires for high-performance devices on large areas. *Microsystems & Nanoengineering* 4, (22). Dahiya, A.S., Christou, A., Neto, J., *et al.*, 2022a. In tandem contact-transfer printing for high-performance transient electronics, *Advanced Electronic Materials* 8, 2200170.

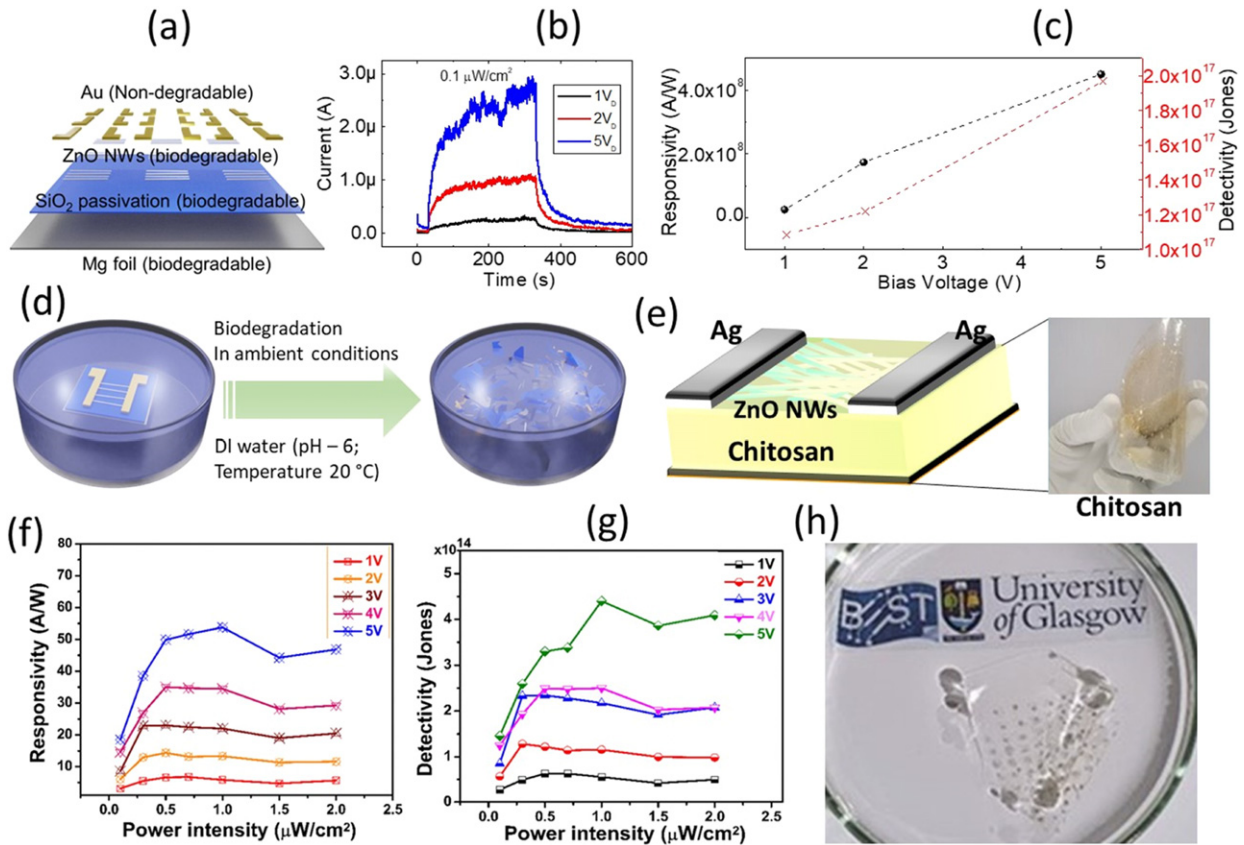


Fig. 5 Biodegradable photodetectors using ZnO NWs. (a-d) In-tandem contact transfer printing-based photodetectors: a) exploded view illustration of various biodegradable and nonbiodegradable layers, b) response to UV light intensity of $0.1 \mu\text{W cm}^{-2}$ and (c) responsivity and specific detectivity at different applied biases, and (d) schematic representation of the biodegradation behaviour of the printed PDs on Mg foils in aqueous solution. (e-h) Spray coated ZnO NWs based photodetectors: (e) Schematic and an optical image of the fabricated device, (f) responsivity, (g) detectivity, and (h) biodegradability test of as fabricated device showing degradability in DI water and PBS solution. Reprinted from Yalagala, B. P., Dahiya, A.S., Dahiya, R., 2023. ZnO nanowires based degradable high-performance photodetectors for eco-friendly green electronics. *Opto-Electronic Advances* 6, 220020. Dahiya, A.S., Christou, A., Neto, J., *et al.*, 2022a. In tandem contact-transfer printing for high-performance transient electronics, *Advanced Electronic Materials* 8, 2200170.

subjected to the same single UV illumination-dark cycle. The obtained coefficients of variation for decay time and current on/off ratio were $< 15\%$ and $\sim 28\%$, respectively, showing the uniformity in the sensing response (Fig. 4 (c)).

Contact printing was also employed for the heterogeneous integration of Si and ZnO NWs on a commercial polyimide film, to obtain UV photodetectors (García Núñez *et al.*, 2018a). In this work, contact printed ZnO NWs constitute the photoresistive load in a Wheatstone bridge circuit. The Wheatstone bridge configuration provides higher sensitivity compared to voltage dividers and can self-compensate environmental effects, as temperature, humidity, and mechanical stress. In this circuit (Fig. 4 (d)), Si NWs constitute the fixed resistors, while ZnO give the variable light-depending resistance. To fabricate this circuit, two successive patterned contact printing steps were carried on the receiver polyimide substrate. For each NW printing step, the receiver was differently patterned with the photoresist, so that each NW species was printed only in the pre-defined region of the substrate according to the circuit. This route allowed the selective heterogeneous integration of different NW materials for a NW-resistor based circuit. Connections and electrodes in the circuit were fabricated via photolithography route. The resulting photodetectors showed high on-off current ratios and, owing to the Wheatstone bridge configuration, low dark current variation in the tested temperature range of $20\text{--}80^\circ\text{C}$ (Fig. 4 (e)). Under bending, the flexible photodetectors showed constant dark current in both tensile and compressive conditions and identical dynamic photoresponse curve in different tensile bending conditions (radii of curvature in the range $5\text{--}20\text{ mm}$).

The in-tandem contact transfer printing of ZnO NWs was also employed to fabricate flexible UV photodetectors (Dahiya *et al.*, 2022a). In this case, all-printed photodetectors were fabricated wherein high-resolution electrohydrodynamic printing was employed to define source-drain Au electrodes (Fig. 4 (f)). The two-terminal I-V showed rectifying device behaviour (Fig. 4 (g)). Despite a low on-off current ratio (~ 9), the resulting all-printed NW-based photodetectors showed extremely high responsivity ($8 \times 10^7 \text{ A W}^{-1}$, on par with the best ZnO-based device and record-high among the printed ones) and specific detectivity ($8 \times 10^{16} \text{ Jones}$) (Fig. 4 (h-j)). This can be attributed to the small device area, excellent charge transport

within the highly crystalline ZnO NWs grown via Vapour Phase Transport and low impurity level maintained with a dry printing process. Considering their time-resolved photoresponse, these devices present a good repeatability among cycles, with rise and recovery times of 15 s and 30 s, respectively. Along with the photo-induced liberation of free electrons, these characteristic photoresponse times are also due to the lowering and rise of the energy barriers at the metal electrode-NW interface. Indeed, the Au (work function of -5.1 eV) electrodes printed on top of the ZnO NWs (electron affinity of ~ 4.5 eV) form Schottky contacts and the upward band bending of NWs in dark conditions contributes to increase the barrier height at the interface. In UV illumination condition, the decrease of NW surface charges lowers the barrier and further contributes to the increase of device on-current. This mechanism can be exploited to have higher on-off current ratios: increasing the charge concentration in the NWs, the height of the metal-semiconductors barriers decreases, and higher on/off ratios are obtained. NW doping is compatible with the transfer process, as it can be easily carried before they are printed on the flexible substrate. Another method to increase the current on-off ratio is to increase the number of NWs in the channel. However, this is more challenging as the density of NWs transferred is unavoidably lower than the contact printed layer. This is because it is very challenging to achieve 100% efficiency during the NW pick-up and NW transfer steps. To account for this, in the study of in-tandem contact-transfer printing, the pick-up efficiency was increased via the capillary-force assisted NW adhesion: evaporating a thin layer of water on the surface of the stamp, the capillary forces developed at the stamp-NW interfaces during the NW pick-up temporarily increase the NW adhesion to the stamp (Ma *et al.*, 2017). The water layer only acts as a temporary glue as, when it evaporates, no additional force hinders the release of NWs on the target substrate. Further, it was found that higher stamp-target substrate contact forces during transfer increase the transfer efficiency although still not 100%.

Biodegradable UV Photodetectors

Wearable electronic patches/tattoos that can be applied on clothes or directly on skin could be used for UV exposure monitor. In this regard, progress has been made to develop disposable sensors. However, disposable does not mean biodegradable and thus enhancing the problem of electronic waste. In tandem contact-transfer printing technique has been used to fabricate ZnO NW based photodetectors on a biodegradable substrate as well (Dahiya *et al.*, 2022a). Towards this, photodetectors were printed on biodegradable Magnesium (Mg) foils (≈ 20 μm thick) as device substrate (Fig. 5 (a)). The Mg foils were passivated by depositing ~ 1 μm thick biodegradable SiO_2 using the plasma-enhanced chemical vapour deposition (PECVD) technique. The time resolved photoresponse was measured at the constant UV intensity 0.1 $\mu\text{W cm}^{-2}$ for different bias voltages (Fig. 5 (b)). Based on the time-resolved photoresponse curves, R , D^* , EQE , and $I_{\text{Light}}/I_{\text{Dark}}$ ratio values were extracted. Increasing the bias voltage from 1 to 2–5 V progressive increase of the R and D^* (Fig. 5 (c)) was observed. After performance evaluation, device transience behaviour was studied. For this, the photodetectors were placed inside de-ionised (DI) water ($\text{pH} \approx 6$) at room temperature (Fig. 5 (d)). Under these conditions, the etching rate of the device (mainly Mg) is ≈ 83 nm day^{-1} . With this rate, the complete dissolution of the Mg foil would occur after ≈ 240 days. To enhance the etching rate solution with higher basicity or temperature (36 – 37 $^\circ\text{C}$) could be used. A faster transience of ZnO photodetectors was achieved by changing the device substrate to chitosan. In this work, photodetectors based on ZnO NWs spray coated electronic layer on a chitosan substrate was proposed (Fig. 5 (e)) (Yalagala *et al.*, 2023). Chitosan was chosen because of the exciting material properties such as has mechanical flexibility, chemically stable and transparent, and it dissolves in water into non-toxic components. In this way, by integrating these photodetectors with fabrics, they could be harmlessly biodegrading while washing. The adopted fabrication route is eco-friendly, resource-efficient, and scalable. First, the chitosan films were casted from aqueous solution and then, the Ag electrodes (150 $\mu\text{m} \times 200$ μm) were defined on top of the films via screen printing. Finally, ZnO NW were spray coated on top of the printed electrodes, obtaining a NW mesh in an active device area of 0.03 mm^2 . A schematic illustration of the device is shown in Fig. 5 (e). The constructed devices show a high current on-off ratio of 4×10^3 and they exhibit a repeatable and stable photo response with a linear current increase for a significant range of UV light intensities (0.1 – 2.0 $\mu\text{W/cm}^2$). Considerable responses are also shown by illuminating low UV intensities (0.1 $\mu\text{W/cm}^2$). The devices capability to detect low light intensities is explained by the large number of highly crystalline, high aspect ratio NWs in the sensing channel. Indeed, the devices present high responsivity (> 55 A W^{-1} , Fig. 5 (f)) and excellent specific detectivity (4×10^{14} Jones, Fig. 5 (g)), especially among biodegradable photodetectors. These high values were achieved because of: (i) metal-NW Schottky contacts, and (ii) many NW-NW junctions along the channel. In dark conditions, each of the NW-NW interface energy barriers contributes to lower the device's dark current. Further, the sudden change in NW-NW junction resistances also explains the fast response (0.7 s) and recovery (0.8 s) times.

Given their transient nature, it is important to test if these biodegradable devices operate in a stable manner under ambient conditions. Therefore, performance retention must be characterised under the thermal, and mechanical stresses. In terms of expected temperatures, the wearable UV photodetectors are expected to work in ambient temperature, which varies depending on the geographical location and season. The chitosan substrate photodetectors show repeatable temporal photo response in the tested range of temperatures (15° – 45°C), proving the device stability in common ambient temperatures. Concerning the photo response variation at different temperatures, a small increase of I_{dark} is observed, supposedly because of an increase of the thermionic current at increasing temperatures. Instead, the on current does not show any appreciable change, which is explainable thinking that the loss of carrier mobility occurring at higher temperatures counterbalances the increase of thermionic current. Therefore, the responsivity values remain relatively constant when temperature is varied. Further, since the wearable devices are expected to work under different bending conditions, the photodetectors robustness and reliability was tested by measuring the

photo response under different bending states. In particular, the temporal response characteristics were collected with the substrate bent at different curvature radii (40 mm, 20 mm, and 10 mm) with the devices subject to tensile stresses. It results that the devices are sufficiently stable, although an appreciable decrease in the responsivity was observed for smaller curvature radii. This can be explained thinking that when the devices are stretched, there is an increase of the NW-NW junction resistances.

Concerning their biodegradability, the wearable devices disintegrated first into the device constituents and then partly dissolved at room temperature in DI water within 20 min (Fig. 5 (h)). Indeed, the chitosan substrate quickly absorbs water and once swollen, it starts to physically disintegrate, as water easily hydrolyses the glycosidic bonds in the polysaccharide structure. Then, the functional groups in the structure (as hydroxyl, amino, carbonyl and amido groups) react with water to produce first oligosaccharides and, from it, glycoproteins, both non-toxic species. Degradability studies were also conducted with immersion in phosphate buffered saline solution with pH 7.4, which closely matches the properties of biofluids. In this case, full substrate biodegradation was attained in less than 2 days. The longer degradation time is explained by the lower chitosan solubility rate in basic environments. With the substrate biodegradation, the NWs get completely dispersed in water, while the Ag electrodes were left floating.

Conclusion

This chapter presented different ZnO NWs based flexible and transient photodetectors. For devices which require direct metal contacts at the both ends of NWs, the possibility to minimise the device-to-device variability depends on the uniformity of NW density, dimensions and orientation, especially when large-scale fabrication is targeted. Indeed, all these features contribute to the number of NWs directly contacted in a device and the level of orientation, particularly, in the probability to have NW-NW contacts. If the NWs can be grown uniformly with lower distribution in diameter variation, our opinion is that contact printing and drop-on-demand printing technique could be attractive resource and energy efficient routes to realise such photodetectors over large substrate area. Both lithography-patterned contact printing (García Núñez *et al.*, 2018a) and in-tandem contact-transfer printing (Dahiya *et al.*, 2022a) allowed NW printing over selected locations of the substrate and, thus, hetero-integration of nanostructures was possible (Christou *et al.*, 2023). However, both printing routes could disturb the contact printed layer or affect the NW alignment. For example, the wet processes steps involved in photolithography are seen to reduce the NW density and disturb their orientation, while possibly leading to NW contamination. In the in-tandem contact-transfer approach, the transferred NW array has lower density than the parent contact printed one. Further, NW orientation is affected due to the use of elastomeric stamp during their transfer. Overall, comparing the two approaches for heterointegration of nanostructures, in-tandem contact-transfer printing appears more suitable, as it does not require wet steps that may contaminate the structures, whereas lithography-patterned contact printing requires a new photolithography route for each different NW species to be contact printed. In terms of resource efficiency, contact-transfer approach does not generate chemical wastage, unlike its lithographic counterpart, and also makes better use of the grown NWs, as the contact printed array used as source of aligned NWs can be reused for multiple transfers (provided stamp-source registration). Further the absence of lithographic steps in the contact-transfer route makes the process scalable to areas bigger than the conventional wafers.

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Heterodyne and Phase Sensitive Plasmonic Terahertz Detectors and Spectrometers

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Abstract

Short channel Field Effect Transistors (FETs), such as modern Si Complementary Metal Oxide Semiconductor (CMOS) FETs, operate in ballistic or quasi-ballistic transport mode when the electron inertia and oscillations of the electron density in the device channels – called plasma waves – become very important. Such transistors could detect or mix the frequencies of the terahertz (THz) or sub-THz radiation impinging on the device or the FET integrated circuit. Operating such devices and circuits in homodyne, heterodyne, and phase-sensitive regimes could enhance their responsivity by orders of magnitude and enable the THz line-of-sight detection, THz spectroscopy, and frequency-to-digital conversion applications. This technology could support future 6G communications in the 240–320 GHz range for orders of magnitude enhancement in data communication speed and bandwidth.

Key Points

- Increasing demand for bandwidth is fueled by explosive growth in internet use, Wi-Fi communications, and Internet of Things applications
- These bandwidth demands make the transition to the 240–320 GHz band (in the atmospheric window for terahertz absorption) inevitable in the near future (3–5 years).
- Modern transistors, such as Si CMOS with 20 nm and below feature sizes (including 3 nm, 2 nm, and 1 nm technology nodes) could operate as TeraFETs in resonant or damped plasmonic modes.
- TeraFETs could detect and process THz signals at frequencies up to at least 5 THz (for Si CMOS technology) or even higher.
- Operating TeraFETs and circuits in homodyne, heterodyne, and phase-sensitive regimes could enhance their responsivity by orders of magnitude and enable the THz line-of-sight detection, THz spectroscopy, and frequency-to-digital conversion applications.
- The killer application of this technology is 6G, including Wi-Fi 6G.

Introduction

Increasing demand for a larger bandwidth provides a strong incentive for communications in sub-terahertz (sub-THz) or even THz band. The feature sizes of transistors, including Si MOSFETs, have shrunk to dimensions smaller or comparable with the mean free path even at room temperature, and these devices operating in sub-THz and THz frequency ranges are often referred to as TeraFETs (Shur *et al.*, 2019) (see Fig. 1).

The electron inertia in such short channel devices is important and the electron transport becomes ballistic (Shur and Eastman, 1979) or quasi-ballistic (Shur, 1981). In this regime, the oscillations of the electron (or hole) density in the device channels (i.e., plasma waves) become an important factor determining the devices response to impinging radiation. As mentioned above, the transistors operating in this regime (Dyakonov and Shur, 1996a,b) are often referred to as TeraFETs. Plasmonic Si (Knap *et al.*, 2004; Stillman *et al.*, 2011; Pala *et al.*, 2005), GaAs (Lu *et al.*, 1998; Lu and Shur, 2001; Knap *et al.*, 2002a), GaN (Knap *et al.*, 2002b; El Fatimy *et al.*, 2006; Peale *et al.*, 2009), and graphene (Bandurin *et al.*, 2018; Zhang and Shur, 2021; Grigorenko *et al.*, 2012; Ju *et al.*, 2011), TeraFET detectors have demonstrated tenability (Knap *et al.*, 2002a; El Fatimy *et al.*, 2006; Tauk *et al.*, 2006) low values of the noise equivalent power (Kurita *et al.*, 2014), and very high modulation frequencies (up to hundreds of GHz) (Kachorovskii and Shur, 2008; Shur *et al.*, 2017a; Ryzhii *et al.*, 2018). These detectors operate at zero bias or could be driven by the drain-to-source current that increases their responsivity but also increases the flicker noise (Lu and Shur, 2001; Liu *et al.*, 2020a; Veksler *et al.*, 2006). TeraFETs have been used in focal plane arrays (Pfeiffer and Ojefors, 2008; Schuster *et al.*, 2011; Lissauskas *et al.*, 2012) TeraFETs have also been used as frequency mixers (Dyakonov and Shur, 1995; Harter *et al.*, 2016; Ryzhii *et al.*, 2014; Satou *et al.*, 2004).

In this article we discuss the heterodyne (Gershgorin *et al.*, 2008; Shur *et al.*, 2017b; Ning Wang *et al.*, 2016; Wang *et al.*, 2019; Lin *et al.*, 2019; Grzyb and Pfeiffer, 2015; Yuan *et al.*, 2019), or the homodyne (Veksler *et al.*, 2007; Rumyantsev *et al.*, 2017; Ikamas *et al.*, 2021), detection scheme could further dramatically enhance the TeraFET performance. We also analyze using phase detection to design a TeraFET spectrometer (Shur *et al.*, 2017b; Liu *et al.*, 2020b, 2021a) and ratchet effect detector (Rupper *et al.*, 2018; Rozhansky *et al.*, 2015; Olbrich *et al.*, 2016) and enable line-of-sight TeraFET detection.

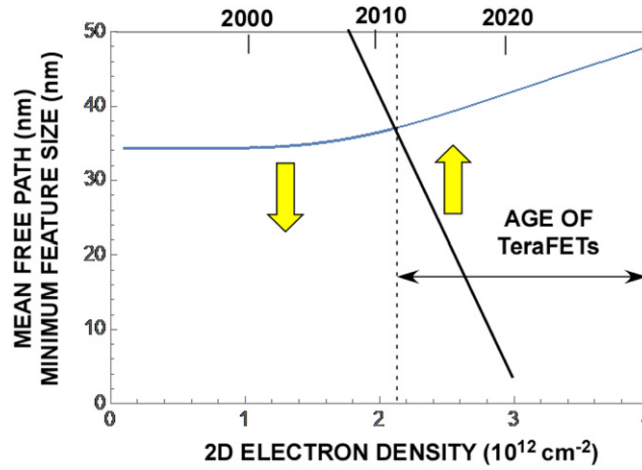


Fig. 1 Mean free path in Si MOS at 300K for electron mobility of 1450 cm²/Vs versus 2D electron density and MOS minimum feature size versus time.

Background/Fundamentals

Homodyne and Heterodyne Detection

Fig. 2 illustrates the heterodyne and homodyne detection operation. It shows an incoming signal with an amplitude U_a and frequency ω mixed with a strong signal from a local oscillator with the amplitude U_b ($U_b \gg U_a$) and a frequency $\omega + \Omega$ ($\Omega \ll \omega$). The amplitude of the resulting signal with the low intermediate (beat) frequency Ω is proportional to $U_a U_b$. Therefore, a strong local oscillator signal enhances the output signal. And the resulting lower (beat) frequency makes the output amplification or processing much easier compared to the straight THz signal amplification.

As was shown in (Gershgorin *et al.*, 2008; Shur *et al.*, 2017b; Ning Wang *et al.*, 2016; Wang *et al.*, 2019; Lin *et al.*, 2019; Grzyb and Pfeiffer, 2015), such homodyne and heterodyne detectors could be realized using nonlinear rectification and two-dimensional (2D) plasma-wave effects in TeraFETs. TeraFET detection uses the rectification of the ac voltages induced between the device contacts. In ballistic or quasi-ballistic short channel TeraFETs, plasmonic resonances could dramatically enhance the detection responsivity. Moreover, the amplitude of the resulting beat signal can be further drastically increased by an electric current flowing in the transistor channel due to an increase in the nonlinear properties of the channel.

Fig. 3(a) shows an implementation of the homodyne detection in the sub-THz range (Rumyantsev *et al.*, 2017, Shur *et al.*, 2017b). In this case, a beam splitter was used to provide a weak signal and a strong local oscillator signal. **Fig. 3(b)** shows the detection enhancement due to the homodyne regime.

In the homodyne detection, the two sources of THz or sub-THz radiation impinge on a TeraFET: $U_1(t) \cos(\omega t + \varphi)$ (measured signal) and $U_2 \cos(2t_{\text{local oscillator}})$. The amplitude of the measured signal could be slowly modulated at a low frequency, fm (typically, in the range of 50 Hz to 1 MHz). This modulation allows using a lock-in amplifier to improve the signal-to-noise ratio.

As shown in Gershgorin *et al.* (2008), the rectified homodyne signal V_r for the non-resonant detection depends on the phase difference φ between the signals:

$$V_r = \frac{1}{2} \frac{U_1 U_2 \cos \varphi}{\sqrt{U_{gt}^2 + U_{gt}^2/2}} \quad (1)$$

Here $U_{gt} = U_{gs} - U_T$ is the gate voltage swing, U_{gs} is the gate-to-source voltage, and U_T is the threshold voltage of the TeraFET. As seen from Eq. (1), the response depends on the phase difference between the measured and local oscillator signal.

The analytical theory of the TeraFET heterodyne detection was developed by Gershgorin *et al.* (2008). Eqs. (2) and (3) present the key result of the heterodyne detection theory. For the above threshold regime, when $U_{gt} = U_{gs} - U_T \gg k_B T/q$, where k_B is the Boltzmann constant, T is temperature, and q is the electronic charge,

$$V_{r\Omega}(t) = \frac{1}{2} \frac{U_1 U_2 \cos[\Omega(t - t_{oa}) + \varphi]}{U_{gt} \sqrt{1 - I/I_{sat}}} \quad (2)$$

Here $t_{oa} \sim \frac{L^2}{\mu U_{gt}}$ is the characteristic electron transit time across the TeraFET channel, μ is the low field mobility, I is the drain-to-source current and I_{sat} is the drain-to-source saturation current. As seen in **Fig. 4**, this analytical theory is in good agreement with the results of the numerical simulations.

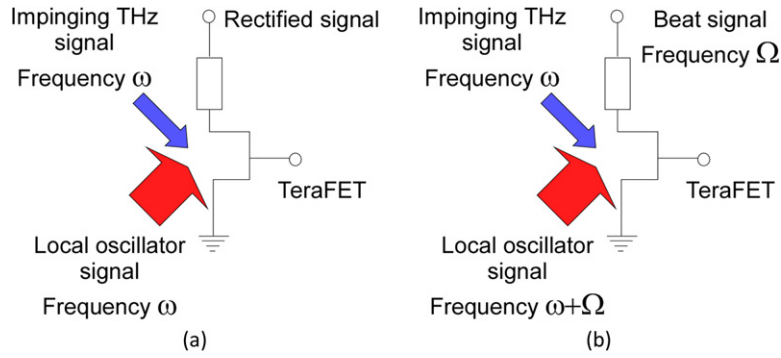


Fig. 2 (a) Homodyne detection; (b) Heterodyne detection operation: an incoming signal with an amplitude U_a and frequency ω is mixed with a strong signal from a local oscillator with the amplitude U_b ($U_b \gg U_a$) and a frequency $\omega + \Omega$ ($\Omega < \omega$).

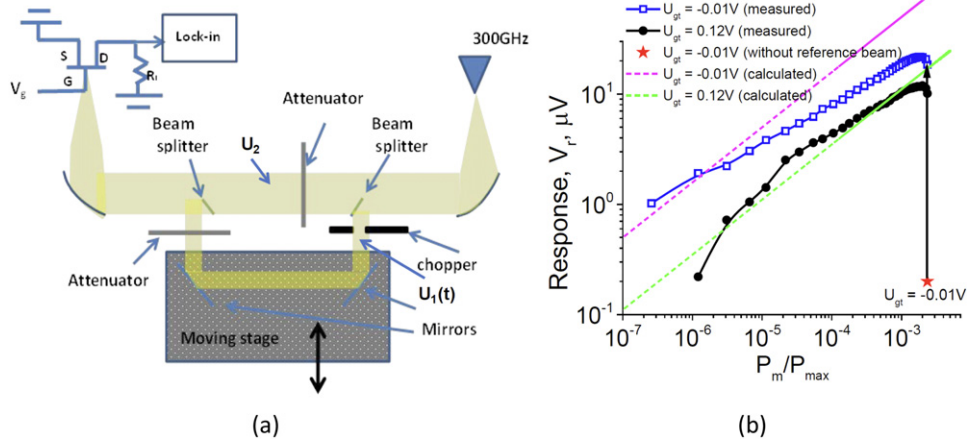


Fig. 3 (a) Homodyne detection setup for detecting attenuated 300 THz radiation; (b) Homodyne response as a function of the modulated beam power, P_m . Reproduced from Shur, M.S., Liu, X., Rummyantsev, S., Kachorovskii, V., 2017b. Heterodyne phase sensitive terahertz spectrometer, In: Proceedings of 2017 IEEE Sensors Conference, pp. 621-623, 978-1-5090-1012-7/17/\$31.00 © 2017b IEEE.

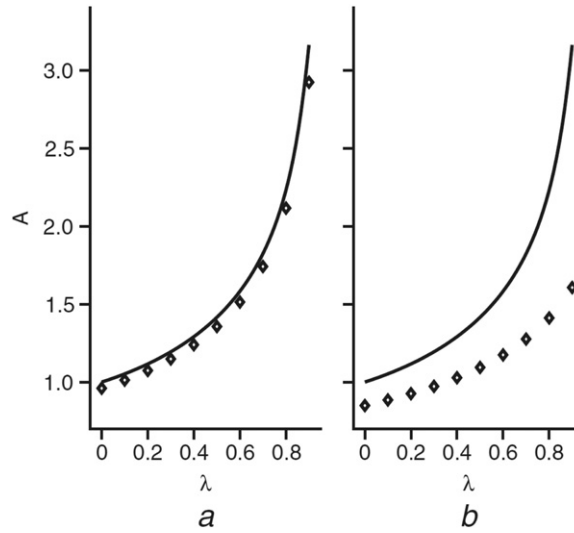


Fig. 4 Amplitude of the heterodyne signal (measured in the units $U_1 U_2 / 2 U_{gt}$) as a function of the drain-to-source current (measured in the units of saturation current) for $\omega / \Omega = 32$ (solid line analytical theory, diamonds represent the results of numerical simulations): (a) for relatively small amplitudes of the incoming signals, $U_1 / U_{gt} = 0.02, U_2 / U_{gt} = 0.1$, excellent agreement of the analytical theory with numerical simulations is observed in the whole range of currents; (b) the same for higher amplitudes of the incoming signals, $U_1 / U_{gt} = 0.2, U_2 / U_{gt} = 0.7$. From Gershgorin, B., Kachorovskii, V.Y., Lvov, Y.V., Shur, M.S., 2008. Field effect transistor as heterodyne terahertz detector. Electronics Letters 44 (17).

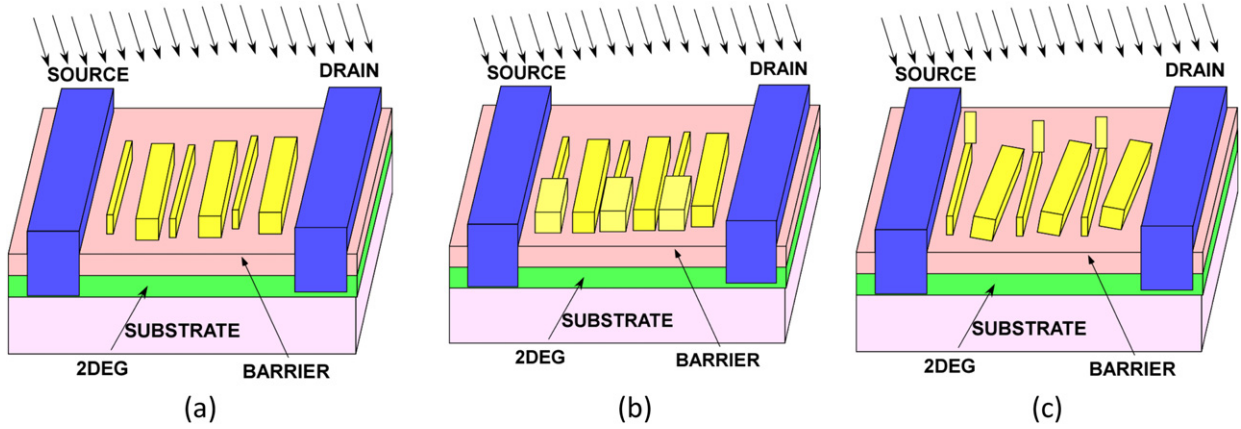


Fig. 5 Asymmetrical ratchet patterns using grating gate structures.

For the below threshold regime, when $U_{gt} < 0$ and $q|U_{gt}|/k_B T > 1$

$$V_{r\Omega}(t) = \frac{1}{2} \frac{qU_1 U_2 \cos[\Omega(t - t_{ob}) + \varphi]}{\eta k_B T \sqrt{1 - I/I_{sat}}} \quad (3)$$

Here $t_{oa} \sim \frac{qL^2}{2\mu k_B T}$, k_B is the Boltzmann constant, T is temperature in degrees Kelvin.

The key result is the phase sensitivity of the TeraFET homodyne and heterodyne detector signal. Such a dependence of the TeraFET response on phase enables other applications, including “ratchet” detection, THz spectroscopy, frequency-to-digital conversion, and line-of-sight detection.

Ratchet Detection

The ratchet TeraFET detectors use periodically modulated asymmetrical structures, such as asymmetrical dual grating gate devices (see Fig. 5(a)). As a consequence of their spatial asymmetrical modulation (see Fig. 1(a)) the electric field in the 2DEG is (Rozhansky *et al.*, 2015)

$$E_x(t, x) = E_{ax} \exp(j\omega t) [1 + h_x \cos(q_\omega x + \varphi)] \quad (4)$$

Here ω is the frequency of the impinging radiation, E_x is the electric field in the 2DEG in the ratchet structure, E_{ax} is proportional to the square root of the intensity of impinging radiation, q_ω is the wave vector of the spatial modulation of the 2DEG, parameter h_x describes the effect of the spatial modulation on the electric field in the 2DEG, and the phase angle q_ω , the phase angle φ accounts for the periodic ratchet structure asymmetry. Eq. (4) applies for linear polarized radiation for the case when the phase shift is in the x -direction. For elliptically polarized radiation and more complex asymmetrical patterns shown in Fig. 5(b) and (c), a more general equation describes both x - y -components of the electric field:

$$\vec{E}(t, x, y) = \vec{E}_0 \exp(j\omega t) [1 + \hat{h} \cos(q_\omega x + \varphi)] \quad (5)$$

(The matrix $\hat{h}$ has only diagonal components h_{xx} and h_{yy} for the ratchet structure of the type shown in Fig. 5(a) and (b)).

Just as a single TeraFET, the ratchet structure has a resonant response at the plasma frequencies. However, the width of the response depends on the inverse Maxwell relaxation time and is much smaller than the inverse momentum relaxation time. This is a big advantage of the ratchet structures for resonant detection applications.

TeraFET Spectrometer

Further generalization of using the phase for the THz detection is using the interference between the plasma waves excited at the source and the drain of a TeraFET. When the impinging signal drives two antennas shifted by phase (see Fig. 6(a)) the response drops to zero at a certain frequency that is determined by the plasma wave transit time and, therefore, on the gate bias. Fig. 6(b) shows the response of a single TeraFET spectrometer as a function of frequency. This response derivative could be dramatically enhanced by using a dc bias and circuits using several TeraFETs.

A larger response and a more accurate frequency determination could be achieved using current-driven TeraFET spectrometers (Liu *et al.*, 2021a). These spectrometers could be also used for frequency-to-digital conversion (Liu *et al.*, 2021b).

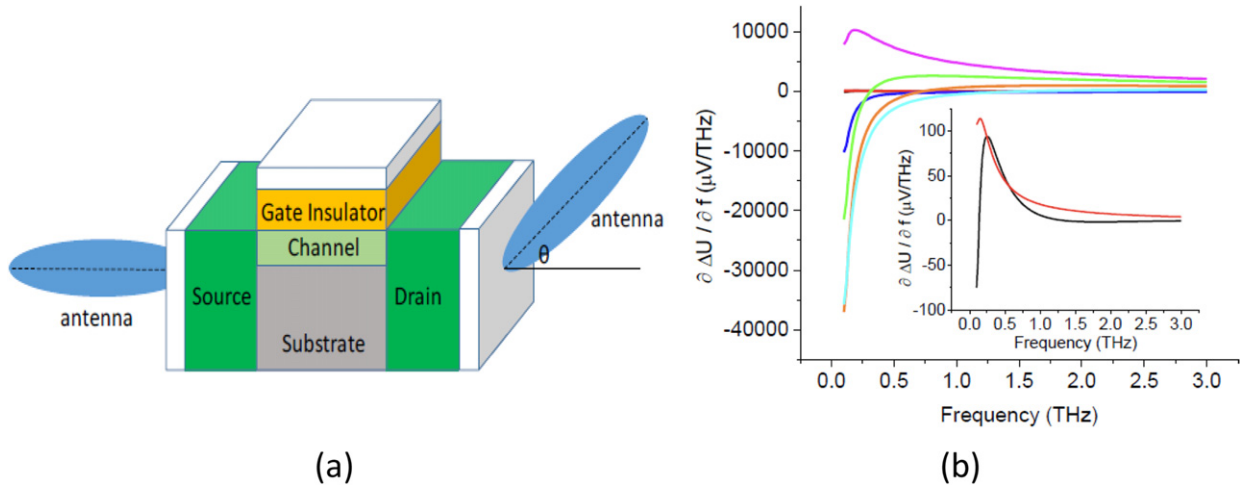


Fig. 6 TeraFET spectrometer schematics (a) and the derivative of the simulated spectrometer response as a function of the THz signal frequency for different THz signal configurations (b). Reproduced from (a) Liu, X., Ytterdal, T., Shur, M., 2020b. Plasmonic FET terahertz spectrometer. IEEE Access 1–6 <https://doi.org/10.1109/ACCESS.2020.298227516>. (b) Liu, X., Ytterdal, T., Shur, M., 2021. Design and Optimization of TeraFET spectrometer. In Proceedings of the 2021 IEEE International Conference on Microwaves, Antennas, Communications and Electronic Systems (COMCAS), Tel Aviv, Israel, 1–3 November 2021; pp. 477–481. © IEEE 2021.

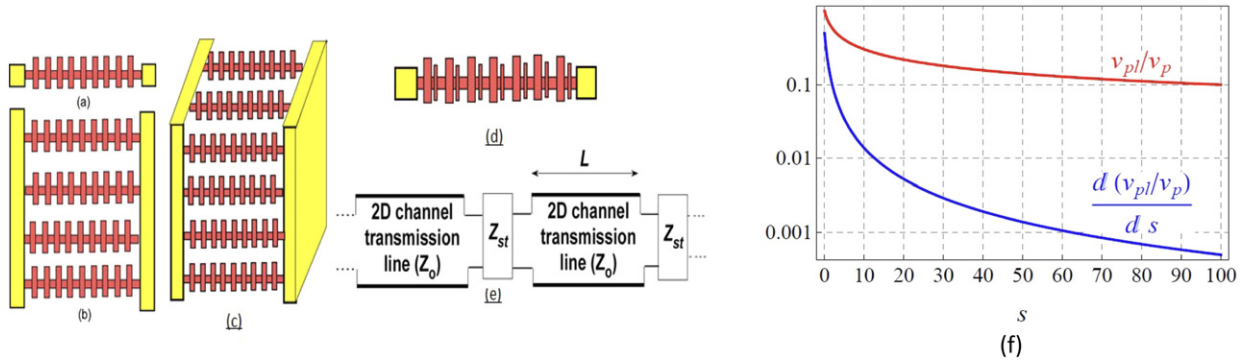


Fig. 7 Schematic of the stub plasmonic crystals. (a) 1-D. (b) 2-D. (c) 3-D. (d) 1-D asymmetric stub plasmonic crystal. (e) Equivalent transmission line electric circuit for the 1-D stub plasmonic crystal variable width TeraFET structures, and plasmon velocity v_{pl} (red) and dv_{pl}/ds (blue) as a function of the effective stub area, s , in the 1-D plasmonic stub crystal. Reproduced from Aizin, G.R., Mikalopas, J., Shur, M., 2019. Plasmons in ballistic nanostructures with stubs: Transmission line approach, IEEE Transactions on Electron Devices 66 (1), 126–131. <https://doi.org/10.1109/TED.2018.2854869>, <https://arxiv.org/abs/1806.00682>. © IEEE 2020.

Phase-Driven Detection in Variable Width TeraFET Arrays

Phase relations play a crucial role in variable-width TeraFET structures (Aizin *et al.*, 2019, 2020, 2018, 2016) (see Fig. 7). Such structures could be used for detection, generation, and frequency conversion. The phase control in these structures is achieved using plasmonic stubs, which are narrow protruding strips that play a role of a shunting impedance and could be used to adjust the phase between the sections. Fig. 7(f) shows a high sensitivity of the plasmon velocity to the effective stub area that could be adjusted by the stub gate bias. This is very important for optimization of the plasmonic terahertz devices. The plasma velocity could be considerably slowed down, which makes it much easier to achieve the conditions of the plasma boom instability (Aizin *et al.*, 2016) to be used for generating sub-THz and THz radiation.

Conclusions

Modern ultra-short field effect transistors operate in the sub-THz and THz frequency ranges, where ballistic and quasi-ballistic transport and the resonant or overdamped plasma waves play a crucial role. Such devices – referred to as TeraFETs – have found

applications as detectors, mixers, and frequency multipliers of the THz and sub-THz radiation. The heterodyne, homodyne, and phase-sensitive regimes of TeraFET operation enhance responsivity, enable new applications, and will find applications in 6G communications (including Wi-Fi 6G) and THz sensing applications.

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Antennas as Sensors

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Abstract

The chapter describes the rationale, the basic concepts and the reference configurations for the "antenna-based sensors". The review includes real examples and case studies given by the state-of-the-art scientific literature.

Key Points

- Antennas can serve both communications and sensing purposes by sensing the nearby environment.
- Sensing can be performed by dedicated sensors or bare antennas. In the second case the sensing mechanism can be three: unmodulated sensing, modulated sensing, and sensing by auto-tuning antennas.
- Variations in the phenomenon to be sensed can be transduced in variations of the electromagnetic properties of antennas.

Introduction

The antenna is an interface device working as a transducer between a guided wave and a propagating one. From another perspective, the antenna can convert the energy carried by a time-varying current over its body into energy carried by waves traveling in a medium and vice-versa.

Antennas are mainly used to communicate, detect far emitters (radioastronomy), track moving targets (radar) and convey high-power energy into an object (heater and jammer). However, they can also be used as a key module of a sensing system wherein the change of a physical quantity to be measured is converted by the antenna in a change of an electromagnetic property revealed from the remote.

An antenna is the terminal part of any transmitter/receiver system. Its performance is characterized by electric parameters, namely the input impedance versus frequency when looking toward the circuit, and the radiation gain and the effective length versus angle and frequency, when looking toward the propagation medium. When an antenna is in touch with or placed close to an external object made by dielectric or metal, the local boundary conditions that the antenna sees are modified by the electromagnetic coupling with that object, and the current distribution on the antenna will be reshaped. Accordingly, the antenna parameters will change so that the measured radiation will carry information about said antenna/object interaction. Hence, the antenna act as a transducer from a chemical/physical process, involving a change of local boundary conditions close to the antenna itself to a measurable variation of an electromagnetic response.

The observable antenna's parameter(s) providing information about what is happening in the proximity is one (or more) of the following:

- (i) the resonance frequency,
- (ii) one or more between strength, phase, and angular distribution of the radiated or reflected field,
- (iii) power delivered to a load in case of receiving antennas.

The kinds of sensing mechanisms described above can be exploited directly in an analog way, involving a continuous-wave regime, without any electronic component attached to the antenna. Instead, the sensing modality can be mediated by the use of a local modulator, thus enforcing a modulated regime by using a microchip transponder on board, even if no additional sensing device is used. Accordingly, three families of sensing mechanisms exploiting an antenna will be addressed next:

- (i) unmodulated sensing,
- (ii) modulated backscattering sensing,
- (iii) sensing by auto-tuning antennas.

The third sensing family can be considered an evolution of the second one by using a new paradigm of integrated circuit (IC) transponders with a multi-state dynamic impedance. A further sensing family resorts to dedicated sensors, uses the antenna only for communications, and will not be addressed in the following.

For each transduction mechanism, the rationale and application examples are reported here together with the achievable resolution and accuracy.

Background and Fundamentals

Antennas are inherently sensitive to the change of the background medium. For instance, in the case of a homogeneous space-filling material with magnetic and dielectric parameters ($\mu = \mu_0 \mu_r$, $\varepsilon = \varepsilon_0 \varepsilon_r$), the input impedance Z_A of the antenna is a shifted and scaled replica with respect to that in the air according to the Deschamps equation:

$$Z_A(\omega, \varepsilon, \mu) = \sqrt{\frac{\mu_r}{\varepsilon_r}} Z_A(\sqrt{\mu_r \varepsilon_r} \omega, \varepsilon_0, \mu_0)$$

with $\omega = 2\pi f$

In general, antenna features, namely the radiation gain $G(\theta, \varphi)$, directivity $D(\theta, \varphi)$ and input impedance Z_A , depend on the current distribution along the conductor layout but also on their interaction with the surrounding environment. Currents spread along with the antenna shape according to its electrical length, the latter being proportional to the wavelength $\lambda = c/f$, with c speed of the electromagnetic wave into the surrounding medium. If the medium changes, e. g. the permittivity varies from air $\varepsilon = \varepsilon_0$ to $\varepsilon = \varepsilon_r \varepsilon_0$, the speed of the electromagnetic wave changes and the wavelength is accordingly scaled by $\lambda = c/(\sqrt{\varepsilon_r} f)$. Consequently, the electrical length of the antenna modifies with an impact on both impedance and directivity. The same principle also holds in the case of modification of antenna shape since the current distribution undergoes variations.

Furthermore, the gain $G(\theta, \varphi) = \eta D(\theta, \varphi)$ depends on the radiation efficiency η defined as the ratio between the radiated power P_R and the total power entering the antenna $P_{in} = P_R + P_J$, where P_J is the power loss. When the material surrounding the antenna changes, e.g. with modification in the imaginary part of its complex permittivity, the interaction with the antenna current produces a variation of the lost power P_J , and, consequently, of the gain.

Let us denote with $\Psi(t)$ a time-varying physical, chemical, or geometrical parameter of the environment surrounding the antenna and let us consider the Friis' formula describing the radio link between two antennas placed at a given distance d in polarization alignment. Antenna A is affected by the parameter $\Psi(t)$ in evolution, while antenna B is in rest condition. Then, the power delivered to antenna B, assumed as perfectly matched to its load, by antenna A is:

$$P_{A \rightarrow B}[\Psi] = \left(\frac{\lambda}{4\pi d} \right)^2 P_{in} G_A[\Psi](\theta, \varphi) \tau_A[\Psi] G_B(\theta, \varphi)$$

In particular, the power radiated by antenna A depends on the radiation gain and the power accepted by the antenna itself, quantified by the power transfer coefficient

$$\tau_A[\Psi] = \frac{4R_G R_A[\Psi]}{Z_G + Z_A[\Psi]^2},$$

where $Z_G = Z_G + jX_G$ is the impedance of the transmitter.

Accordingly, any modification in gain or the input impedance of antenna A is turned into a variation of the transmitted power and can be hence retrieved by antenna B through a proper analysis of the received signal in amplitude and phase.

Unmodulated Sensing

In the case of un-modulated sensing, the bare electromagnetic response of the antenna (namely its resonance frequency and the angular distribution of the radiated field) is used to earn information about changes happening in the close vicinity of the antenna itself.

Such changes can be due to different phenomena. In particular, changes in the position of nearby objects and in their status (i.e., damage/composition) can be monitored. Examples of each of these classes will be given next.

Unmodulated sensors have the benefit of extremely low cost due to the absence of any electronic component. On the other hand, they exhibit a very limited specificity to the process to be monitored. Though a proper design will manage to achieve good sensitivities to specific phenomena, it cannot fully remove the uncertainty produced by further (disturbing) phenomena in the sensor environment.

Sensing of Displacements and Deformations

The change of the mutual position between antenna and object to be monitored will impact the antenna response by modifying the antenna's near-field environment. Similarly, if the antenna is placed onto the object to be monitored and this moves away from other objects in the environment, such a movement can be detected from remote.

For instance, multiple antennas placed on the sides of a crack on a wall can act as crack sensors: a displacement of the first antenna, attached on one side of the crack, with respect to a second antenna on the other side, will result in an indirect measurement of the crack evolution (Rizzoli *et al.*, 2009). The operating principle used in this case is based on the dependence of the array radiation on the inter-element distance. As a matter of fact, two antennas acting as a broadside phased array (hence excited with the same phase and amplitude) having an inter-element distance in the range of $]0.5; 1.5[$ wavelength, will have first-

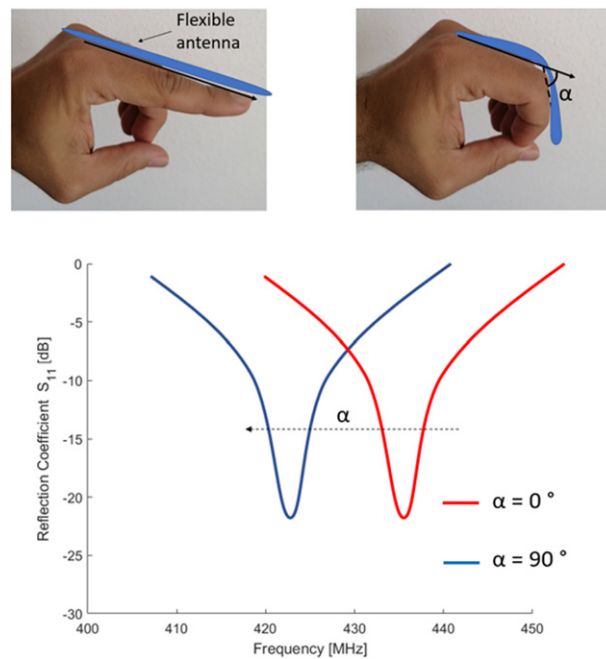


Fig. 1 Concept of an antenna as sensor for finger posture (top). Changes in the finger bending will cause variations in the frequency response of the antenna's reflection coefficient (bottom). Adapted from Su C.H., Wu H.W., 2019 An antenna sensor to identify finger postures. In: Proceedings of the IEEE Eurasia Conference on IoT, Communication and Engineering (ECICE), 571–574.

order nulls away from the broadside direction. The angular position of these nulls is dependent on the actual distance between the antennas. By measuring the shift in the null position, the mutual distance of the elements can be estimated.

If a flexible sensor is wrapped onto the object to be monitored and the shape of said object varies, this will be detectable thanks to the fact that also the shape of the antenna/sensor itself will have changed. For example, finger posture sensing can be obtained based on this mechanism (Su and Wu, 2019) by measuring the reflection coefficient of an antenna being bent (Fig. 1). The antenna is, in this case, printed on flexible material and attached to a finger. The finger movement will change the mutual position of two portions of the antenna, thus affecting the frequency profile of the reflection coefficient.

Sensing of Changes in the Health Status of the Object

The object to be monitored might be prone to changes in its status, such as damages, cracks, holes, as typical of metallic structures for aerospace applications or concrete structures for construction applications. The development of this damage, for instance, in terms of crack propagation, can be seen as a change of the status of the object and, accordingly, of an antenna placed over it. For instance, a metallic plate can be monitored (Mohammad and Huang, 2011) by printing a patch antenna on a substrate and using such metallic plate as the ground layer. Suppose the crack propagates in the metallic plate; the antenna's current distribution will be modified, resulting in a frequency shift in the reflection coefficient of the antenna, measurable by connecting a Vector Network Analyzer (VNA) to the antenna itself or wirelessly through the measurement of the radar cross-section (RCS) of the antenna.

Sensing of Changes in the Composition of the Object

Let us suppose that the chemical/physical composition of the object (or medium) in the proximity of the antenna changes, for instance, due to humidity absorption, freezing or other phenomena impacting the dielectric properties of the object/medium. In that case, the antenna will experience a different effective electromagnetic permittivity around it, ultimately causing a variation in the antenna response, as suggested by the Deschamps equation. This mechanism can be exploited (Vena et al., 2016) to turn a chipless tag into a humidity sensor (Fig. 2).

Chipless tags are a specific class of unmodulated sensors, as they are composed of metallic parts only, without embedding any silicon chip. The radar signature they produce (due to their specific design) is used to extract a unique identifier. By integrating a sensing material onto the chipless tag, sensing capability can be achieved. For instance, silicon nanowires are known to have a good sensitivity to humidity.

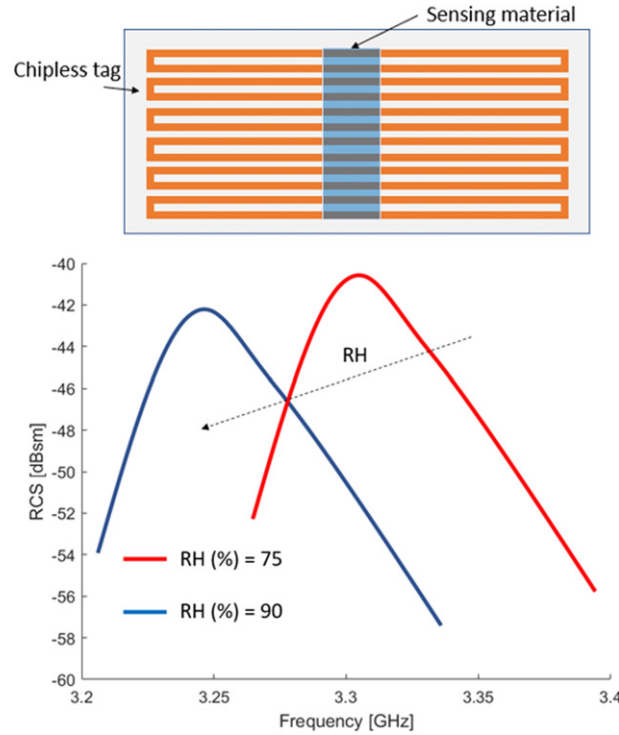


Fig. 2 Concept of chipless tags with humidity sensing material in the middle (top). Changes in the environmental humidity will cause variations in the frequency response of the antenna's radar cross-section (bottom). Adapted from Vena, A., Perret, E., Kaddour, D., Baron, T., 2016. Toward a reliable chipless RFID humidity sensor tag based on silicon nanowires. *IEEE Transactions on Microwave Theory and Techniques* 64 (9), 2977–2985.

Then, measuring the radar cross-section of the tag via an external antenna, the change in the relative humidity of the environment can be estimated through the analysis of the frequency shifts of the RCS peaks.

Sensing Through Modulated Backscattering

Modulated backscattering is a communication architecture in which a backscatter node, i.e. the *tag*, comprising an antenna and an integrated circuit, broadcasts information to an illuminator, i.e., the *reader*, by modulating and reflecting back the incident electromagnetic wave coming from the reader itself. The modulation, and consequently the reflection, is due to an intentional mismatch between the antenna and the IC impedance that generally varies among two high/low values, corresponding to the symbols of the coded information. At the reader side, the sequence of the transmitted bits can be retrieved by properly demodulating the reflected wave. The communication link is hence asymmetric: the forward reader-to-tag link is mainly aimed at exciting the tag and is characterized by high carried power. The backward tag-to-reader link is instead in charge of data transmission with power levels extremely low, being only a fraction of the impinging signal.

Modulated backscattering is currently implemented by Radiofrequency Identification (RFID) platforms. Well assessed in logistics for labeling, tracking and tracing goods and procedures, RFID is being increasingly adopted also for sensing purposes. Indeed, data transmitted back to the reader during the interrogation protocol are digitally encoded, but the strength of the backscattered power is impressed in an analog manner by the antenna configuration, the interaction with nearby objects, by the propagation modality, and even by the mutual position and orientation among the reader and the tags. Compared with unmodulated sensing, such an approach is more robust and effective since the reflected wave bringing the sensing information can be easily recognized and processed by the reader so that multiple sensors can be interrogated simultaneously.

RFID platforms can be deployed in both short-range (namely HF/NFC systems working at 13.56 MHz) and long-range (working in the UHF 860–960 MHz frequency band) systems. In the former case, the interaction with the reader is mostly one-to-one (inductive coupling), whereas in the latter case, information can be contemporarily broadcasted among a single reader and hundreds of tags, being the radiating elements of conventional antennas operating in far-field conditions. Antenna-as-sensor paradigms mainly apply to UHF RFID.

During a typical RFID communication, in addition to the Electronic Product Code (EPC) that univocally identifies the tag, reader and tag share different types of data:

- (i) *Received Signal Strength Indicator* (RSSI), that is related to the reverse communication link, i.e. to the power backscattered by the tag toward the reader $P_{R \leftarrow T}(\Psi)$ and hence to the differential radar cross-section, Δ_{RCS} ,

- (ii) *phase*, $\varphi(\Psi)$ of the signal backscattered by the tag and related to the differential radar cross-section among the two modulating states,
- (iii) *turn-on power*, $P_{in}^{to}(\Psi)$ that is the minimum power the reader must emit to wake up the tag, and that is an indicator of the direct link.

RSSI and turn-on power can be further combined to drop out the influences of the distance and the reader's and tag's gains and orientations. A propagation-independent indicator denoted as the *Analog Identifier* (AID) can be hence defined (Marrocco, 2011).

The previous parameters are strictly related to the tag antenna operating features and can be used as data inversion curves between the measured data and the evolution $\Psi(t)$ of the process:

$$\{P_{R \leftarrow T}, P_{in}^{to}, \varphi, AID\} \longleftrightarrow \Psi(t)$$

Any variation of the surrounding environment Ψ able to affect the antenna gain and input impedance is transduced in a variation of the signals transmitted and received by the reader and can be hence related to a sensing activity performed by the tag itself. To remove possible baselines, the above indicators are generally normalized by their value in a particular reference state, say $\Psi(0)$, for instance, collected at the time of the tag's placement into the environment to be monitored. In this way, differences in the signals are evaluated rather than their absolute values. The sensing parameters can be collected at a fixed frequency or within the whole RFID band to provide integral metrics suitable for capturing macroscopic variations of the sensor-antenna response over frequency, such as the detuning and the attenuation or magnification of the response.

Two approaches can be defined to implement the sensing activity: (i) *bare antenna*, the sensing capability of which is only related to the natural sensitivity of an antenna to time-variant boundary conditions, and the (ii) *loaded antenna*, in which the sensing features depend on specific chemical and mechanical sensors integrated into the antenna structure as variable loads.

Bare Antenna

A bare antenna, with nothing else on board, can be exploited as a natural permittivity sensor for the remote discrimination of kind, amount and distribution of liquids (Fig. 3), powders, and biological processes (Occhiuzzi, et al., 2013). The sensing activity (Fig. 3) requires analyzing the variation of the reverse communication link, e.g., the backscattered power of one or more tags attached to the container that have been matched in case of specific compounds (Marrocco and Amato, 2009; Capdevila, et al., 2011). For the monitoring of bottle filling, the placement of multiple tags at different levels increases the overall sensitivity to the process by adding an ID modulation. For this purpose, if a tag is tuned for operation in the air, it will not respond when placed in touch with a high-permittivity liquid. Accordingly, by analyzing the set of IDs returned by a vertical array of tags, a discrete estimation of the filling level of the container is achieved.

The same principle holds when the process under observation induces a deformation of the antenna's shape, as in the case of moving surfaces or evolving cracks. The strain can be monitored by a meander-line antenna (Fig. 4). By applying an elongation, its shape will turn from a tightly twisted meander to a zigzag dipole, thus altering the pattern of the currents and hence the antenna's properties, such as the ratio of the actual backscattered power to the backscattered power measured during the steady-state.

A crack can be identified and monitored by using two passive RFID tag antennas placed on top of the crack (Fig. 5) so that its evolution will produce a change of the inter-antenna coupling and, in turn, of the phase of the backscattered field.

Loaded Antenna

A complementary approach to the bare-antenna is the loaded-antenna one, which requires providing the antenna with an external sensing element. This element could be either lumped into a device, connected in some part of the tag's antenna as well as distributed all over the antenna's surface as in the case of chemical-receptor coating. Overall, the sensor is considered as a lumped or distributed impedance loading, $Z_s(\Psi)$, on the tag's antenna. The perturbation of $Z_s(\Psi)$ caused by the change of the environment will accordingly produce a variation of the tag's gain and impedance, wirelessly detectable by measurement of the previously described indicators.

Volatile chemical compounds can be detected by resorting to carbon nanostructures (CNT) paint that is spread over a loop-driven flat dipole (Fig. 6). The device is able to sense the presence of ammonia in the environment, thanks to the absorbing property of the CNT. Changes in the properties of the carbon nanostructures will cause antenna-microchip mismatch and gain variations, readable through turn-on and backscattered power measurements.

Basic information on the motion of the tagged object can be achieved by including a mechanical device onboard the antenna. For instance, a two-chips tag can be connected to one-bit accelerometers (Philipose et al., 2005), made of two mercury switches, each in series with one chip. By mounting the switches in an anti-parallel configuration, a "binary-code-shift keying" is achieved. The identifier ID1 is returned when the acceleration is parallel to the first switch, while the ID2 when acceleration is parallel to switch 2. Such a code-shift keying can also be achieved by resorting to inertial switches, which connect one of the two ICs to the antenna depending on the direction of the movement (Fig. 7) (Occhiuzzi and Marrocco, 2010).

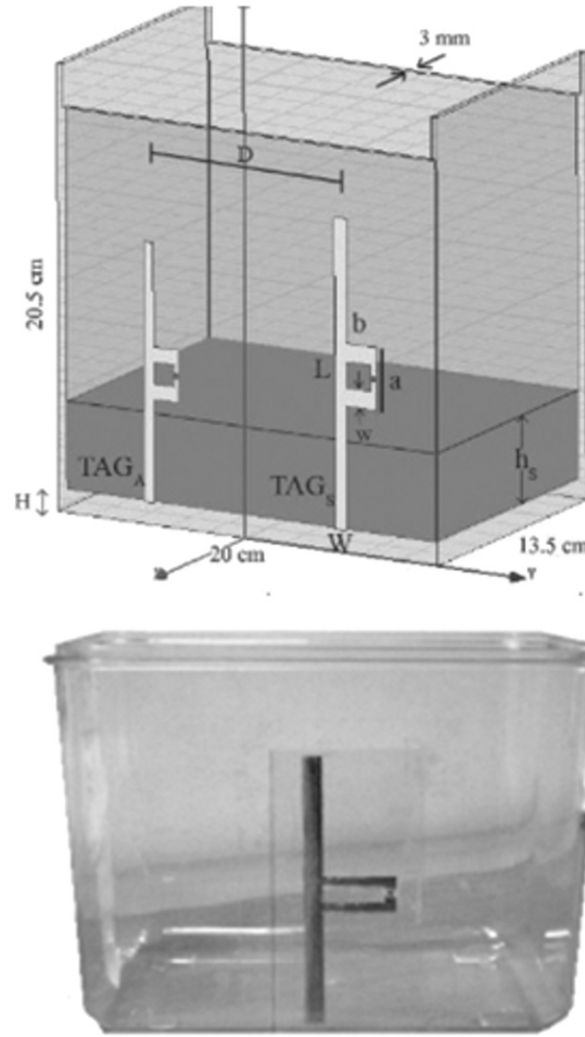


Fig. 3 Bare sensor-antennas for the sensing of filling level. Modified from Marrocco, G., Amato, F., 2009. Self-sensing passive RFID: From theory to tag design and experimentation. European Microwave Conference 1-4.

Design and Usability

Sensing capabilities are generally achieved at the expense of the degradation of the read distance since the changes of physical/chemical features of the environment are sensed by the passive tag through a deviation from its static gain and/or impedance matching. The true effectiveness of the antenna-as-sensor, therefore, is constrained to the tradeoff between sensing and communication.

The optimal configuration of the antenna has to be determined case by case by a synthesis of the sensor-as-antenna response, $\{P_{R \leftarrow T}, P_{in}^{lo}, \varphi, AID\} \leftrightarrow \Psi(t)$, by proper shaping of the geometrical sizes, $A = \{a_1, \dots, a_K\}$, of the antenna or of the eventual loading elements. Such a problem can be formalized as the minimization with respect to A of a multi-objective function, conveniently using a stochastic optimizer, such as the Genetic Algorithm or the Particle Swarm.

The effective capability and the achievable performances in term of precision and accuracy are defined at the system level by considering together tag, reader and communication link. The bare-antenna sensing mechanism is non-specific since the sensed data may be only indirectly related to a physical phenomenon under observation. By loading the antenna with a sensitive element, a more specific and robust response can be instead achieved. Measurement uncertainties, unintentional environmental interactions, misalignments and resolution of readers play a major role in the data accuracy (Fig. 8) (Occhiuzzi and Marrocco, 2016). The environment-independent indicator, such as the analog identifier, revealed to be a more stable and robust metric, even if its dynamic range, and accordingly the corresponding sensing resolution, is generally lower than that of power metrics.

Additionally, data processing can benefit from automatic classification algorithms that can contemporarily manage multiple signals and limit the uncertainties by implementing learned recognition schemes. For example, Fig. 9 shows RSSI measurements regarding ten tags simultaneously read for a given time; such measurements can be exploited for motion sensing through pattern recognition algorithms.

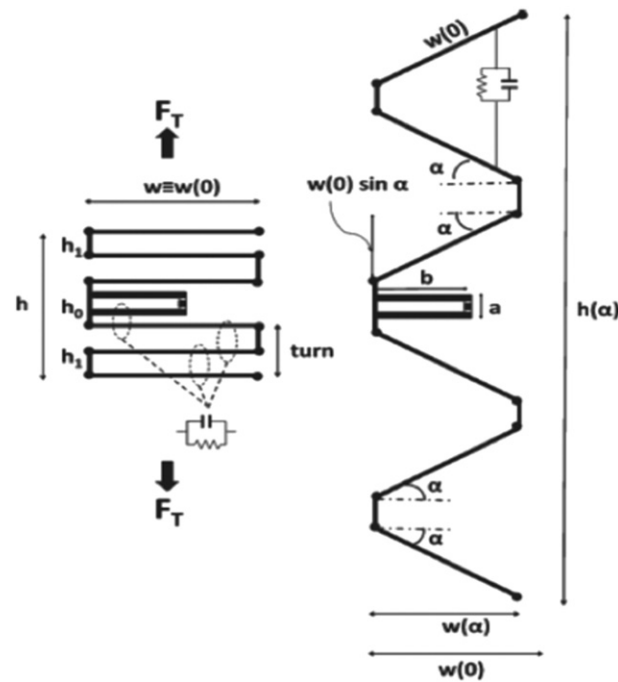


Fig. 4 Meander-line antenna for strain monitoring. From Occhiuzzi, C., Paggi, C., Marrocco, G., 2011a. Passive RFID strain-sensor based on meander-line antennas. *IEEE Transactions on Antennas and Propagation* 59 (12), 4836–4840.

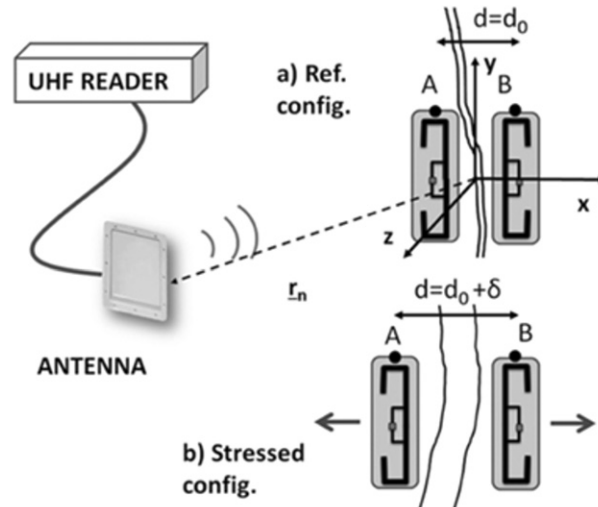


Fig. 5 Crack-sensor composed of two RFID tag antennas. From Caizzzone, S., Di Giampaolo, E., Marrocco, G., 2014. Wireless crack monitoring by stationary phase. *IEEE Transactions on Antennas and Propagation* 62 (12), 6412–6419.

Sensing Through Auto-Tuning Antennas

The uncertainty affecting the antenna-as-sensor measurements due to the propagation channel can be strongly mitigated by exploiting auto-tuning (also known as self-tuning) ICs. An auto-tuning microchip can dynamically change its internal radiofrequency (RF) impedance to match that of the hosting antenna and maximize the power transmission coefficient. Accordingly, it can compensate for changes in the operating environment and preserve the antenna's radiation performance. The IC can also return a digital metric, generally named *sensor code* (SC), which is proportional to the retuning effort and can be employed to sense variations in the boundary conditions. Therefore, auto-tuning-based sensors use the SC for sensing while achieving stable communications thanks to automatic impedance matching.

ICs provided with the auto-tuning feature can be modeled as a resistor connected in parallel with a switchable network of capacitors (Fig. 10(a)) (Caccami and Marrocco, 2018). Accordingly, the equivalent input admittance of the microchip is given by a

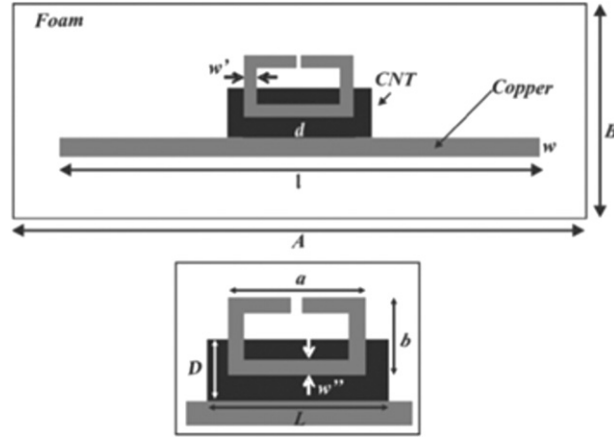


Fig. 6 Chemical-sensing loaded antenna of an RFID tag. The antenna is a loop-driven flat dipole doped with CNT. From Occhiuzzi, C., Rida, A., Marrocco, G., Tentzeris, M., 2011b. RFID passive gas sensor integrating carbon nanotubes. *IEEE Transactions on Microwave Theory and Techniques* 59 (10) (pp. 2674–2584).

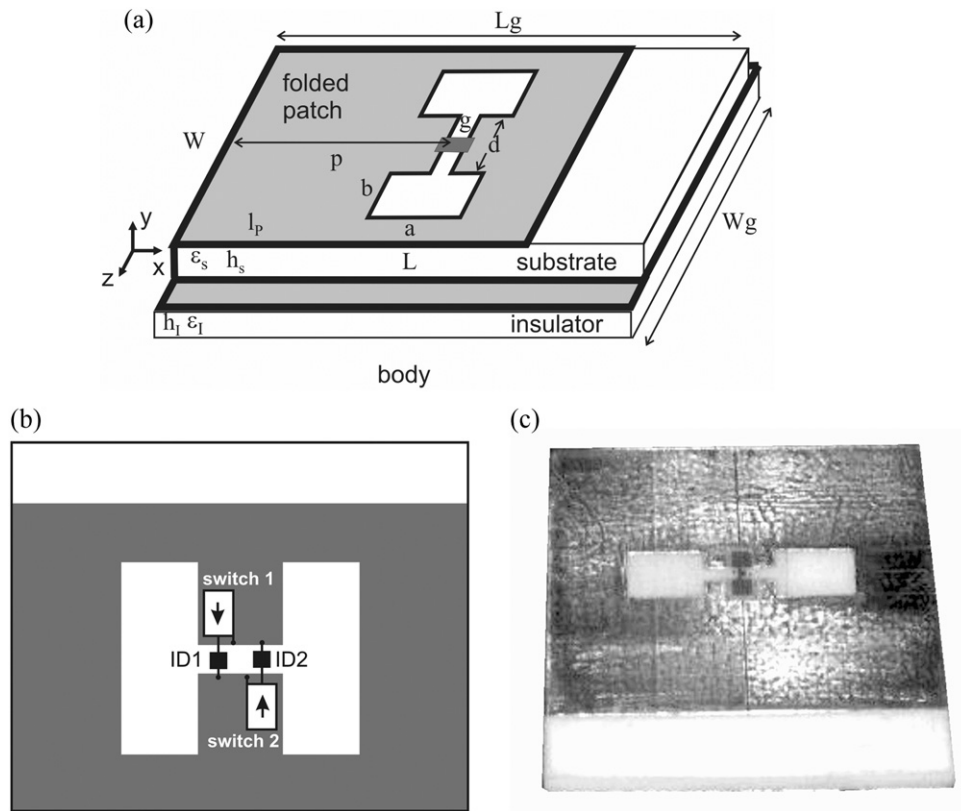


Fig. 7 Antenna integrated with two inertial switches connected with one IC each. One of the two IC is connected based on the movement direction, and the corresponding ID is transmitted. (a) Scheme of the folded patch on the human body, (b) the two inertial switches and the respective direction of actuation, and (c) a sensor-antenna prototype. Modified from Occhiuzzi, C., Marrocco, G., 2010. The RFID technology for neurosciences: Feasibility of Limbs' monitoring in sleep diseases. *IEEE Transactions on Information Technology in Biomedicine* 14 (1), 37–43.

fixed conductance and a variable susceptance:

$$Y_{IC} = g_{IC} + j\omega C_{IC}$$

where Y_{IC} , g_{IC} and C_{IC} are the admittance, the conductance and the capacitance of the chip, respectively. The variable capacitance $C_{IC}(n) = C_{\min} + nC_0$ can span from a minimum value $C_{\min}$ to a maximum value through an incremental step C_0 . The number of equivalent connected capacitors n varies to compensate the antenna's admittance seen by the IC (Y_A) according to the following self-tuning equation:

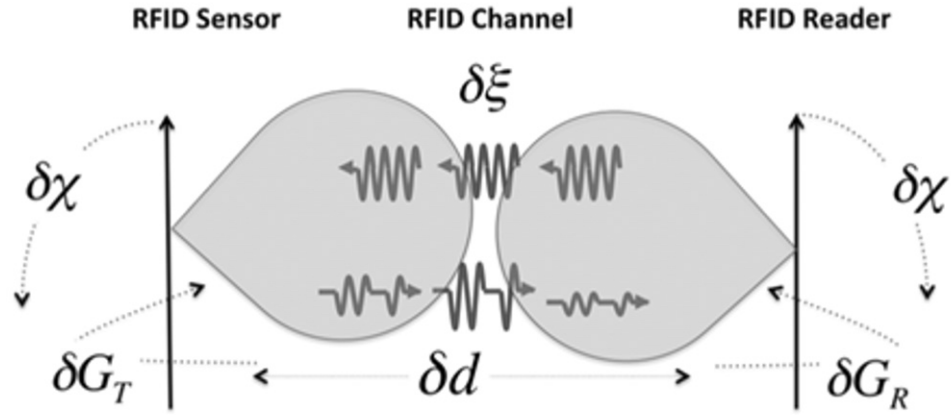


Fig. 8 Components of an RFID platform for sensing purposes (reader, propagation channel and sensor tags). The uncertainty sources $\{\delta G_R, \delta G_T, \delta \chi_P, \delta d, \delta \xi\}$ are the variations on the reader antenna gain, tag antenna gain, polarization, distance, and environment other than the measurand, respectively. From Occhiuzzi, C., Marrocco, G., 2016. Precision and accuracy in UHF-RFID power measurements for passive sensing. *IEEE Transactions on Antennas and Propagation* 16 (9), 3091–3098.

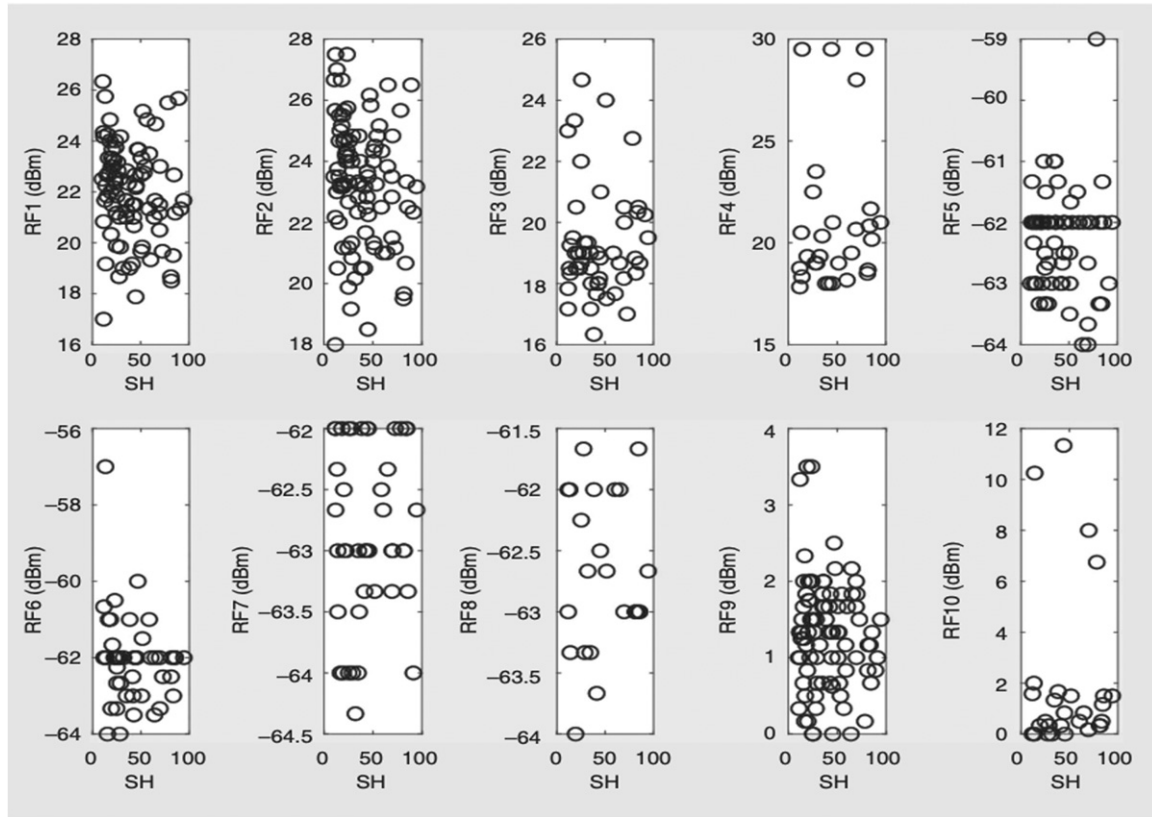


Fig. 9 RSSI measurements from 10 tag antenna simultaneously queried by a single reader for a given period. From Occhiuzzi, C., D'Uva, N., Nappi, S., *et al.*, 2020. Radio-frequency-identification-based intelligent packaging: Electromagnetic classification of tropical fruit ripening. *IEEE Antennas and Propagation Magazine* 62 (5), 64–75.

$$|B_A + B_C| = 0$$

where $B_A = \text{Im}(Y_A)$ and $B_C = \text{Im}(Y_C)$ are the susceptance of the antenna and the IC, respectively. The self-tuning equation achieves the perfect susceptance matching and optimizes the power transmission coefficient.

The auto-tuning antennas can be used for sensing purposes by exploiting the relationship between the antenna admittance and the physical parameter Ψ to monitor. If the auto-tuning IC works in the linear range, the SC value can be evaluated from the antenna susceptance as

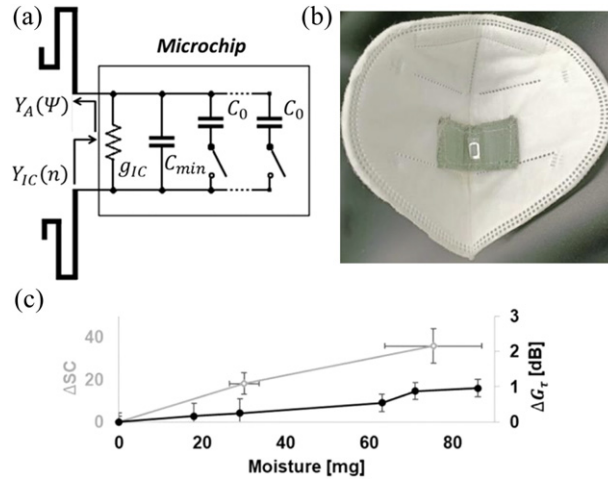


Fig. 10 Modeling of auto-tuning integrated circuits. (a) Equivalent model. From Caccami, M.C., Marrocco, G., 2018. Electromagnetic modeling of self-tuning RFID sensor antennas in linear and nonlinear regimes. *IEEE Transactions on Antennas and Propagation* 66 (6), 2779–2787. (b) Filtering facepiece respirator (FFR) tagged with an auto-tuning antenna-sensor. From Bianco, G.M., Marrocco, G., 2021. Sensorized facemask with moisture-sensitive RFID antenna. *IEEE Sensors Letters* 5 (3), 1–4. (c) Relationship between the Differential SC and the realized gain variations when the moisture inside the FFR increases. Based on (Bianco and Marrocco).

$$SC(\Psi, \omega) = N_{\min} + nint \left\{ -\frac{1}{C_0} \left[C_{\min} + \frac{B_A(\Psi)}{\omega} \right] \right\}$$

where $nint$ is the nearest integer number. The antenna susceptance B_A is unknown; thus, the relationship $SC(\Psi)$ must be experimentally determined through a calibration curve.

Application-specific baselines can be removed by calibrating the sensor code w.r.t. a reference condition Ψ_0 introducing the Differential Sensor Code $\Delta SC(\Psi)$:

$$\Delta SC(\Psi) = SC(\Psi) - SC_0.$$

Auto-tuning antennas are highly susceptible to permittivity changes of the tagged object. For instance, this feature can be employed for estimating the moisture inside a filtering facepiece respirator (FFR) through an appropriate textile substrate. In this way, the antenna acts as a moisture sensor and can sense an excessively wet FFR which may not work anymore (Fig. 10(b,c)) (Bianco and Marrocco, 2021).

Sensing through auto-tuning antennas is possible only if the IC works in given conditions. If the retuning effort is huge or the power delivered to the antenna is excessive, the relationship between the SC and the measurand will be distorted by nonlinear effects that can hinder the sensor effectiveness. Constrained design techniques accounting for the nonlinearities are employed to simultaneously maximize the tag sensitivity and the read range (Bianco, et al., 2020).

Auto-tuning antennas can also be exploited to simultaneously sense two physical parameters, provided that they independently affect the antenna's conductance and susceptance. While the auto-tuning perfectly compensates the susceptance variation, the conductance mismatch causes a reduction of the realized gain $\tilde{G}$. Accordingly, the sensor code and the RSSI will be used to sense a parameter each.

The antenna exploitation as a transducer can be further engineered by resorting to additional transduction mechanisms onboard the antenna, e.g., a humidity-dependent capacitance and a thermal-dependent resistance.

Conclusion

Antennas can be used as low-cost sensors by exploiting their natural electromagnetic coupling with nearby objects. Optimal results are achieved when the antennas are empowered with a battery-less microchip transponder according to the paradigm of Radio-frequency Identification. They can be used where accuracy is not the main issue as they mostly provide qualitative information. However, these devices can be embedded into objects and products and, therefore, they can be exploited over a large scale, thus becoming the building brick of the Internet of Things.

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Recent Developments in Biosensor Technology for Early Diagnosis of Neurological Disorders

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Abstract

Early detection of neurological disorders in humans has posed a critical challenge to the scientific community. The effective diagnosis of the diseases and disorders solely depends on the detection of an imbalance in the concentration of the biomarkers like nucleic acids, proteins, small metabolites, and other biomolecules in the body fluids like blood serum, plasma, urine, etc. In this article, we discuss the topical advancements in design strategies of biosensors with an insight into the trace level detection of disease-specific biomarkers in different biofluids with high specificity and sensitivity enabling early diagnosis of neurological disorders in humans.

Key Points

- To understand the basics of biosensors and their application in the diagnosis of various diseases.
- To provide an insight on the topical advancements in design strategies of biosensors towards a point of care diagnosis of neurological disorders in human
- To discuss the current challenges and developments in the biosensing technology for the early diagnosis of neurological disorders.

Introduction

Neurological disorders are conditions that affect the entire neural system of the human body with a major impact on the brain and spinal cord. The structural, electrical, or biochemical abnormalities in the brain can result in a range of symptoms and can be detected using a parameter known as a biomarker (Hulka *et al.*, 1990). The Biomarkers or the biological markers are the measurable alterations of the biochemical or biomolecules concentrations in any biological medium such as body fluids, tissues, or cells. In recent decades, biomarkers were recognized as potential indicators for various deadly diseases and neurological disorders (Rezaei *et al.*, 2016). The biomarkers can be classified into two types known as biomarkers of exposure and biomarkers of disease (Mayeux, 2004). This classification of biomarkers includes the subclasses named susceptibility, diagnostic, prognostic, and predictive biomarkers (Martin *et al.*, 2015; Wolff *et al.*, 2018; Ren *et al.*, 2018). The susceptibility biomarkers are the indicators of objectively measured environmental agents in the biological system (Kelly and Vineis, 2014). The diagnostic biomarkers are known as the indicators for disease related to disorders in a biological system (Parker *et al.*, 2018). The prognostic biomarkers are the indicators of disease recurrence in a biological system irrespective of the treatment provided (Sechidis *et al.*, 2018). Finally, the predictive biomarkers provide information regarding the response of a biological system to targeted therapy (Ahmadzade *et al.*, 2018). This above-mentioned classification of biomarkers was identified as a sequence of events from exposure to diseases by Perera *et al.* (Perera and Weinstein, 2000). Despite the number of events between exposure and the disease, the biomarkers can also indicate the earliest events in natural history and turn reduce the degree of misclassification (Perera and Weinstein, 2000; Jewell, 2016). A superlative biomarker should be non-invasive, simple, accurate to measure reproducibly, highly related to a biological process of interest, and predictive in the progression of the same (Lemley, 2007). Generally, the anomalous values of the biomarkers in the biological fluids provide the basic information on the development of the irreversible injury and aid the consideration of the pathophysiology of the respective progression (Pandey and Agarwal, 2012). The major examples of the biomarkers comprise pulse, blood pressure over elementary chemistries to the highly multifaceted laboratory examination of biological fluids and tissues (Strimbu and Tavel, 2010).

The recent development in the biomarkers has become more disease-specific which can be used for detection of deadly diseases such as cancers (Chanin *et al.*, 2004; Colomer *et al.*, 2018; Coticchia *et al.*, 2008; Matsuoka and Yashiro, 2018; Henry and Hayes, 2012; Filella *et al.*, 2018) cardiovascular diseases (Dhingra and Vasan, 2017), neurologic disorders (Singh *et al.*, 2018), oxidative stress (Ho *et al.*, 2013), metabolic instabilities such as metabolic syndrome (O'Neill *et al.*, 2016; Srikanthan *et al.*, 2016), diabetic (Dorcely *et al.*, 2017), chronic gout (Stamp *et al.*, 2011), cystic fibrosis (Shoki *et al.*, 2013), etc. The ability of early detection of biomarkers in biological fluids like blood, urine, and plasma would be highly valued for early diagnosis and treatment of any specific diseases. Here the major limitation was observed with the lowest concentration of biomarkers in the biological fluids with various other proteins which pose a great challenge to the current technologies for the detection of biomarkers (Nimse *et al.*, 2016). The wide variety of biomarkers includes antigens, enzymes, deoxyribonucleic acid (DNA), messenger ribonucleic acid (mRNA), amino acids, proteins, etc. The clinical significance of developing a reliable, rapid, cost-effective, and powerful biomarker detection technique has gathered substantial attention of research towards biomarker detection which can effectively assist the process of prognosis, diagnosis, and monitoring of the

recurrence of disease (Hawkrige and Muddiman, 2009). The various conventional techniques developed over a decade for detection of biomarkers were enzyme-linked immunosorbent assay (ELISA) (Lee *et al.*, 2014), surface plasmon resonance (SPR) (Law *et al.*, 2011), mass-sensing biodegradable citrus degreaser (Bio-CD) protein array (Varma *et al.*, 2004), surface-enhanced Raman spectroscopy (SERS) (Li *et al.*, 2013), colorimetric techniques (Wang *et al.*, 2012), electrochemical detection (Labib *et al.*, 2013), fluorescence methods (Rana *et al.*, 2012) and gel-electrophoresis analysis (Lee *et al.*, 2014). These conventional techniques with immunoassays facilitate the detection of targeted biomarkers via capture-antibody functionalization on a solid substrate for target capturing and the assay read-outs. Though these techniques provide a stable quantification of targeted biomarkers in biological fluids, they unanimously grieve some major drawbacks due to the nonspecific adsorption of non-targeted proteins onto the surface of a bio-sensor which impacts the selectivity, sensitivity, and accuracy of the technique (Bolla *et al.*, 2012).

On the other hand, these techniques also require trained manpower, expensive apparatus, and a time-consuming pre-treatment process of the sample. To overcome the vital drawbacks encountered by the conventional biomarker detection techniques, it is indispensable to achieve a low-cost, simple, rapid, highly sensitive, selective, accurate, and portable sensing technique for point of care and clinical diagnostics (Hammond *et al.*, 2016). These predominant requirements of biomarker detection for the clinical diagnostic application were achieved via wide research and development of label-free, chemically modified electrode-based electrochemical biosensors. This article aims to deliver the global development in biosensor technology for the early diagnosis of neurological disorders in humans. It is anticipated that this article will excite a broader research interest in the biosensor for point of care and clinical diagnostic.

Biosensors and Their Types

Biosensors are the transducers that convert the targeted bio-recognition/interaction event into a measurable electrical or optical signal. Characteristically an excellent biosensor should possess high specificity, sensitivity, and reusability (Hammond *et al.*, 2016; Mehrotra 2016). The biosensors can be classified into two types depending on the immobilization process namely, enzymatic and non-enzymatic biosensors. In an enzymatic biosensor, the transducer has been immobilized with an enzyme to produce a signal proportional to the target analyte concentrations (Mulchandani 1998). The non-enzymatic biosensor depends on the redox reaction of the targeted analyte on the surface of the transducer (Gong *et al.*, 2016). Generally, the enzymatic biosensors have been reported with some indispensable limitations like instability and low signal strength derived from the detector biomolecules. Depending on the detection techniques employed for the sensing of biomarkers, the biosensors can be broadly classified into electrochemical biosensors, spectral, electronic, chemiresistive, magneto-resistive, piezoelectric, gravimetric, pyroelectric biosensors, etc (Mehrotra, 2016). This article presents the all-inclusive development of various biosensors and their application in clinical and point of care diagnostic systems for neurological disorders. This section of the article comprises a brief overview of recently reported electrochemical, spectral, electronic biosensors, and other types of biosensors and their working mechanisms.

Electrochemical Biosensors and Their Types

Electrochemical biosensors are the type of transducer in which biochemical information such as analyte concentrations is converted into an equivalent analytical signal such as current, voltage, or impedance. In recent years, electrochemical detection has evolved as a prominent, low-cost, rapid, highly selective, and sensitive analytical technique for biomarker detection (Bolla *et al.*, 2012). Depending on the output analytical signals, the electrochemical biosensors can be classified into three major types namely, potentiometric, amperometric, and impedance analysis. Apart from these classifications, photo-electrochemical biosensors are known for their additional merits such as miniaturization in line with the inherent advantages of conventional electrochemical biosensors and optical biosensors. The process of photo-electrochemical analysis depends on the conversion of electrochemical reactions into electrical signals under light illumination and applied potential. This detection mechanism with an impact of photocurrent generated from the biomolecule oxidation process brings additional merit which has attracted a large scope of research (Hammond *et al.*, 2016). Hence, we discuss more the advancement in the different electrochemical techniques with improved sensitivity and selectivity towards targeted analytes and their applications in various clinical and point of care diagnoses in the following sections.

Potentiometric biosensors

The potentiometric biosensor is the type of electrochemical biosensor incorporating a biological sensing element coupled to an electrochemical potential transducer. These biosensors solely rely on the biochemical/electrochemical reaction (either oxidation or reduction) to form their oxidase or other simpler species which in turn facilitate their detection via electrical potential. Dopamine (DA) is a well-established biomarker for neurological disorders such as Parkinson's disease, attention deficit, schizophrenia, hyperactivity, etc. It is also known as the vital local chemical messenger accountable for communicating signals between the neurons of the brain and the central nervous system (CNS). The imbalance in the level would result in diseases like Alzheimer's, Parkinson's, etc. Krishnan *et al.* (2020) reported a voltammetric electrochemical biosensor for the concurrent detection of ascorbic acid (AA), dopamine (DA), and uric acid (UA) in human urine samples. The hierarchical core-shell metal-organic framework with Ag-doped mesoporous metal-oxide-based hybrid nanocomposites on g-C₃N₄ nanosheets was immobilized onto indium-tin-oxide (ITO) electrode to obtain g-C₃N₄/NC@GC/h-ATS/ITO biosensor. The sensor was reported to enhance sensitivity and

selectivity towards the targeted biomolecules. The improved performance of the sensor was attributed to the synergistic properties of porosity, excellent conductivity, and larger surface area with improved N content. On the other hand, melatonin (MT), is a vital sleeping hormone that is produced in the brain of vertebrates. Generally, the MT is secreted at a high level of concentration at night, and reduced level during the day hours. The MT is reported as a vital hormone in preventing breast cancer, Alzheimer's, insomnia, etc. The imbalance in these hormones could cause deadly diseases like Alzheimer's and cancer, etc. Selvam *et al.* reported a voltammetric electrochemical sensor constructed via immobilization with self-assembled gold nanoparticles (Au NPs) and MoS₂ nanoflakes (NFs) on the glassy carbon electrode (GCE) for the detection of UA and MT in human biological fluids as shown in Fig. 1(a). The developed sensor was reported with high selectivity, reproducibility, repeatability, and excellent stability. The sensor was found successful in the simultaneous determination of UA and MT in the human urine sample with good recovery percentages (Selvam *et al.*, 2020). Henceforth, the Au-MoS₂/GCE electrochemical sensor can be considered an effective platform for the clinical diagnosis of various deadly diseases like breast cancer, Alzheimer's, insomnia, fatigue, etc. In addition to it, Tryptophan (Trp) is an important amino acid precursor for many neurotransmitters and neurochemicals, such as MT and serotonin (ST). Generally, Trp concentration in plasma is reported with a significant correlation with depression, neurological disorders, etc. He *et al.* (2020) reported a potentiometric electrochemical sensor for trace level detection of Trp in biological fluids. The sensor was fabricated via the modification process of GCE with polyvinyl pyrrolidone functionalized graphene (PVP-GR). The PVP-GR/GCE has been reported with a linear range of detection from 0.06 μM to 10.0 μM and 10.0–100.0 μM , and LOD of 0.01 μM . The sensor was observed and reported with excellent repeatability, stability, and selectivity proving it to be an effective platform for detecting Trp in drugs and biological samples.

In general, the Tau protein is one of the vital constituents of the cytoskeleton of the nerve cell. This Tau protein encompassing an amino-terminal region will induce cognitive disorders such as learning, memory, perception, and problem solving, and include amnesia, dementia, and delirium. Tau-441 protein is the longest tau protein isoform used as a biomarker for dementia. Li *et al.* (2020) reported a carbon nanocomposite (CNC) film modified gold electrode sensor for trace level detection of Tau-441 protein in biological samples. Here the CNC comprises multi-walled carbon nanotubes (MWCNTs), reduced graphene oxide (rGO), and chitosan (CS). The biocompatible CS was used as a specific antibody while MWCNTs-rGO had a better conductivity than their counterparts due to the synergy effect. Additionally, AuNPs were used for surface modification of Tau-441 protein for signal amplification. The sensor was reported with a linear range of detection from 0.5 to 80 fM and exhibited a LOD of 0.46 fM. This biosensor was reported successful in the determination of Tau-441 in serum samples collected from 14 normal people, 14 mild cognitive impairment (MCI) patients, and 14 dementia patients with good recovery percentages. These fabrication advancements and the novel sensing techniques have provided a brief insight into the requirement of futuristic potentiometric biosensors aimed at the detection of biomarkers, antibodies, etc., in the human biological fluids such as blood serum, plasma, etc. Wu *et al.* reported the ferrocene-linked gold nanoparticles decorated multiwall carbon nanotubes (FeC-AuNPs-MWCNT) modified SPCE as a sensitive electrochemical sensor for serotonin in human urine samples as depicted in Fig. 1(b). The sensor exhibited high sensitivity and selectivity with a low LOD of 17 nM and a wide dynamic range of detection from 0.05 μM to 20 μM (Wu *et al.*, 2022). Table 1 shows the list of potentiometric-based electrochemical biosensors reported for various biomarker detections in biological fluids for the diagnosis of neurological disorders.

Amperometric biosensors

Amperometric biosensors are transducers that measure the concentration of the targeted analyte/biomarker as a quantitative parameter directly proportional to the electrical current generated via their redox reaction in the medium. These sensors are reported with higher sensitivity, satisfactory stability, and surface renewability. The L-tyrosine is a major precursor of neurological transmitters like DA, catecholamine (CA), norepinephrine (NEP), adrenaline, melanin, thyroid hormones, estrogen, etc. Thereby L-tyrosine can be observed as a potential biomarker for various neurological disorders and chronic diseases. Karthika *et al.* reported a novel cupric oxide decorated on β -cyclodextrin (CuO/ β -CD) nanocomposite modified GCE with Nafion for ultra-selective and sensitive detection of L-tyrosine in blood serum and urine as depicted in Fig. 2(a). The reported CuO/ β -CD/Nf/GCE based amperometry biosensor exhibited a linear range of detection from 0.01 to 100 μM with a high sensitivity of 442 $\mu\text{A}/\mu\text{M cm}^2$ at the operating potential of +0.67 V (vs Ag=AgCl) (Karthika *et al.*, 2020). The LOD of the sensor was reported as 0.0082 μM and it was found successful in trace level determination of L-tyrosine in real-time analysis proving the efficacy of the sensor in bioanalytical applications. Razzino *et al.* have reported an amperometric sensor with enhanced selectivity and sensitivity towards tau protein in biological fluids like human blood plasma, brain tissue extracts, etc. The sensor was fabricated on SPCE using gold nanoparticles and poly(amidoamine) (PAMAM)-nanostructures covalently immobilized onto electro-grafted p-aminobenzoic acid (p-ABA) as shown in Fig. 2(b). Here, the as-fabricated 3D-Au-PAMAM-p-ABA-SPCE was observed with a superior analytical performance towards tau protein in terms of selectivity at the operating potential of –0.2 V (vs Ag=AgCl) in presence of interfering species such as IgGs, HSA, BSA. The sensor exhibited a low LOD of 1.7 pg/mL and reported a successful direct determination of tau proteins in blood plasma and brain tissue extracts from healthy individuals and post mortem diagnosed AD patients with excellent recovery percentages (Razzino *et al.*, 2020). Table 2 displays the list of amperometric electrochemical biosensors reported for the detection of the neurological biomarker in different biofluids for the diagnosis of neurological disorders.

Heavy metal ion sensing

Heavy metal ions (HMIs) are the potential contaminant threats found in biological fluids such as blood serum, plasma, or urine samples. These contaminants enter the human biological system through the food chain and consumption of HMI-contaminated

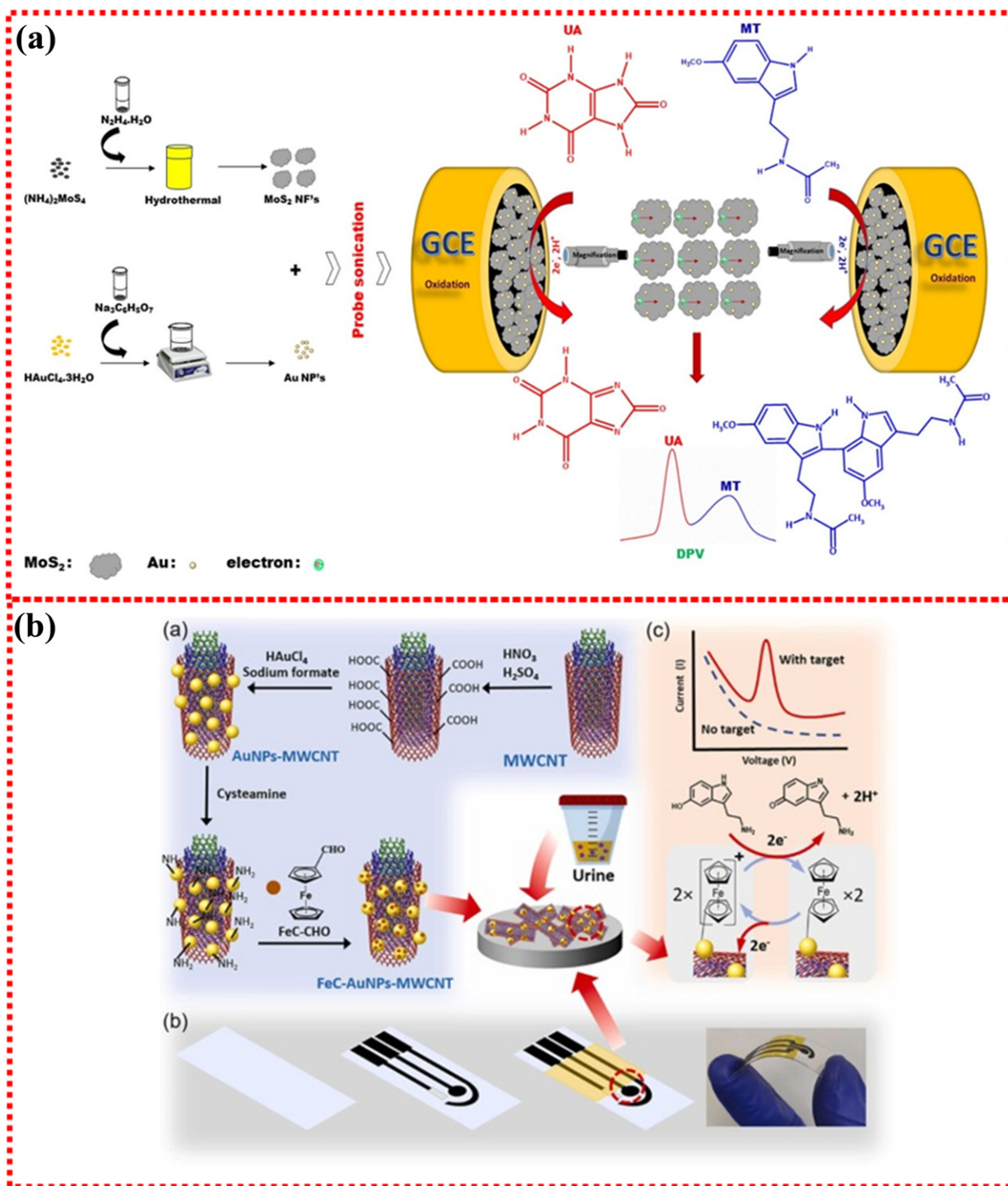


Fig. 1 (a) Schematic illustration of simultaneous detection of uric acid and melatonin based on a self-assembled Au nanoparticle–MoS₂ nanoflake via DPV. (b) Schematics of FeC-AuNPs-MWCNT nanocomposite synthesis and sensor fabrication on flexible SPCE, and 5-HT sensing mechanism. Inset depicts the DPV response of the sensor. Reprinted with permission from (a) Selvam, S., Hansa, M., Yun, K., 2020. Simultaneous differential pulse voltammetric detection of uric acid and melatonin based on a self-assembled Au nanoparticle–MoS₂ nanoflake sensing platform. *Sensors and Actuators B: Chemical* 307, 127683. (b) Wu, B., Yeasmin, S., Liu, Y., Cheng, L., 2022. Sensitive and selective electrochemical sensor for serotonin detection based on ferrocene-gold nanoparticles decorated multiwall carbon nanotubes. *Sensors and Actuators B: Chemical* 354, 131216.

waters. Even the trace level contamination of HMIs in the biological fluids can be determined to cause cancerous disease and neurological disorders. In recent times the metal-induced neurotoxicity has been reported with multiple neurological diseases such as Alzheimer's disease (AD), autism spectrum disorders (ASDs), Huntington's disease (HD), Wilson's disease (WD), Guillain-Barré disease

Table 1 List of electrochemical biosensors reported for diagnosis of neurological disease and disorders via a potentiometric technique.

Working Electrode material	Technique used	Targeted Biomolecule	Disease Diagnosis	Sensitivity	Selectivity studies	Limit of Detection	Dynamic range of detection	Real Sample Analysis – Biological fluids	Ref.
ITO/g-C ₃ N ₄ /NC @GC/h-ATS	DPV	AA	Early diagnosis of Parkinson's disease	208.63A/mM	NaCl, KCl, NaNO ₃ , glycine, histamine, L-cystein, glutamic acid, H ₂ O ₂ , Glu	0.02 M	0.1M - 200 M	Urine	(Krishnan, <i>et al.</i> , 2020)
		DA		1017.54A/mM		0.01 M	2.5 M - 100M		
		UA		110.26A/mM		0.06M	2.5M - 500M		
AuMoS ₂ /GCE	DPV	UA	Neurological disorders	4.6391A/M cm ² #	AA, NaCl, Glu, LA, KCl, DA, urea, AAP	0.0182 μM	0.33 M – 10 M	Urine	(Selvam, <i>et al.</i> , 2020)
		MT		3.8377A/M cm ² #		0.0157 μM			
SnS ₂ /GR-β-CD/GCE	DPV	DA	Neurological disorders	2.49 μA/μM cm ²	HQ, CC, AA, UA, EP, NEP, Chlo	0.004 μM	0.01 M –150.76M	Rat brain, Human blood serum	(He, <i>et al.</i> , 2020)
MWCNTs-rGO-CS-antibody modified Au electrode	DPV	tau-441 protein	Dementia	25.27 μA/fM cm ²	Glu, AA, L-cys,α-Syn, HSA	0.46 fM	0.5 fM- 80 fM	Blood Serum	(Li, <i>et al.</i> , 2020)
FeC-AuNPs-MWCNT/SPCE	SWV	Serotonin	Neurological disorders	1.81 A/M	DA, AA, urea, GLC, UA	17 nM	0.05 – 20 μM	Urine	(Wu, <i>et al.</i> , 2022)

VACNTs – Vertically Aligned Carbon Nano Tubes, PANI – Polyaniline, GO – Graphene Oxide, ITO – Indium Tin Oxide, FTO - Fluorine doped Tin Oxide, PGE – Pencil Graphite Electrode, UA – Uric Acid, DA – Dopamine, AA - Ascorbic Acid, HE4 - Human Epididymis Protein 4, HAS – Human Serum Albumin, BSA – Bovine Serum Albumin, HQ - Hydroquinone, CC - Catechol, EP – Epinephrine, NEP – Norepinephrine, DPV – Differential Pulse Voltammetry, SWV – Square wave voltammetry, SPCE – Screen Printed Carbon Electrode, GC – Glassy Carbon Electrode, GE- Gold Electrode.

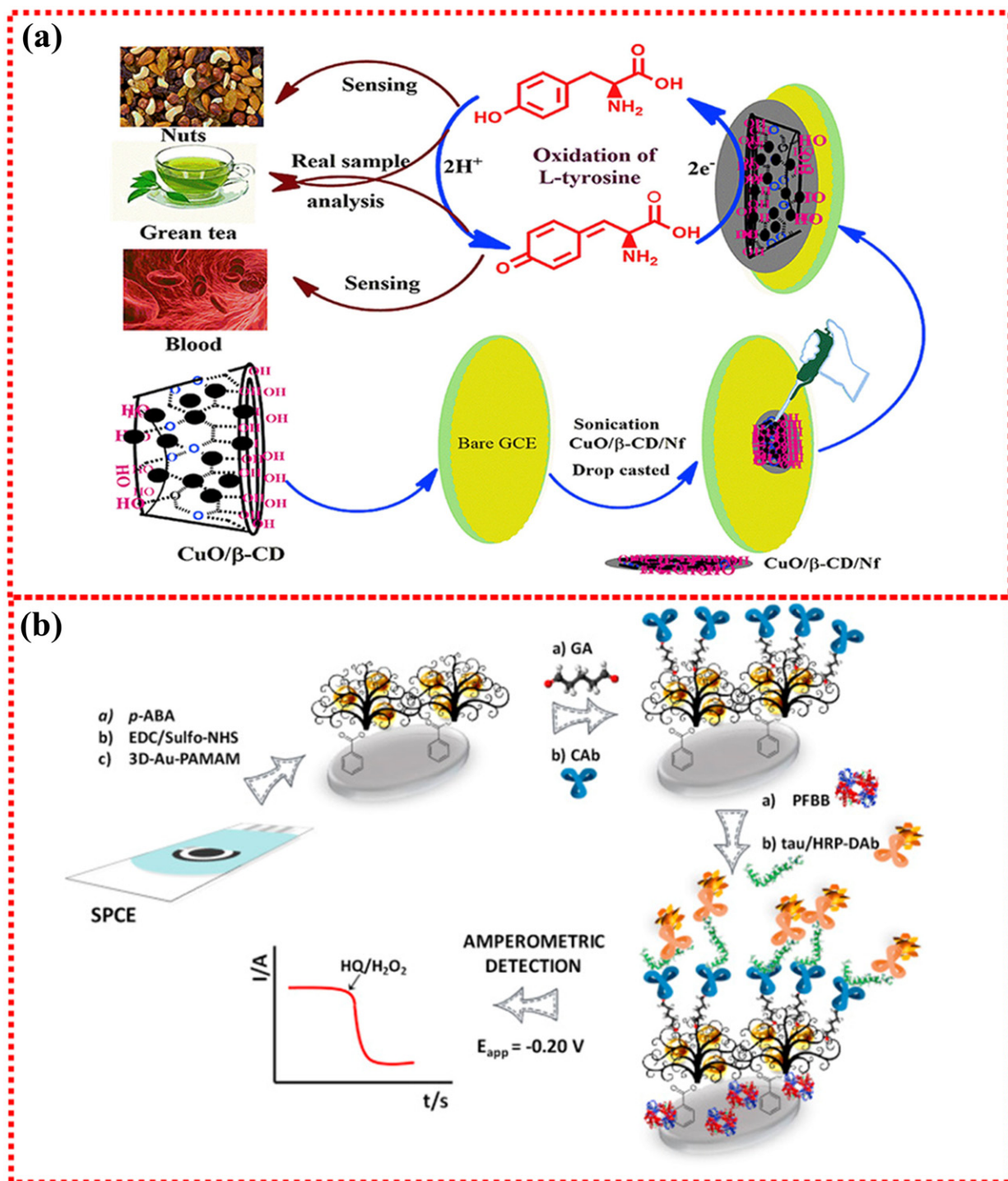


Fig. 2 (a) Schematic illustration of simultaneous detection of uric acid and melatonin based on a self-assembled Au nanoparticle–MoS₂ nanoflake via DPV. (b) Fabrication of HRP-DAB-tau-CAB-3D-Au-PAMAM-p-ABA-SPCE immunosensor for tau protein determination using amperometric transduction. Reprinted with permission from (a) Karthika, A., *et al.*, 2020. Fabrication of Cupric oxide decorated β -cyclodextrin nanocomposite solubilized Nafion as a high performance electrochemical sensor for L-tyrosine detection. *Journal of Physics and Chemistry of Solids* 136, 109145. (b) Razzino, C., *et al.*, 2020. An electrochemical immunosensor using gold nanoparticles-PAMAM-nanostructured screen-printed carbon electrodes for tau protein determination in plasma and brain tissues from Alzheimer patients. *Biosensors and Bioelectronics* 163, 112238.

(GBD), Parkinson's disease (PD), and manganese, multiple sclerosis. The simultaneous detection of HMIs like, Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} in human blood serum was reported using an aluminum ferrite (AFO) nanoflakes modified GCE. The as-fabricated AFO/GCE sensor possessed a distinct oxidation peak potential for all HMIs with peak separation potentials (ΔE_p) of $\sim 0.19 \text{ V}$ (vs $\text{Ag}=\text{AgCl}$),

Table 2 List of electrochemical biosensors reported for diagnosis of neurological disease and disorders via the amperometric technique.

Working Electrode material	Technique used	Targeted Biomolecule	Disease Diagnosis	Sensitivity	Selectivity studies	Limit of Detection	Dynamic range of detection	Real Sample Analysis – Biological fluids	Ref.
SPCE modified with p-ABA, 3D-Au-PAMAM nano-composite and CAb	i-t	tau protein	Alzheimer	-	IgGs, HSA, BSA	0.031 pM	0.11-91 pM	Human plasma and brain tissue extracts	(Razzino, <i>et al.</i> , 2020)
α -Ni _{0.75} Zn _{0.25} (OH) ₂ -modified FTO	i-t	UA	Huntington's disease	-	AA, AM, Lactate, glucose	23 nM	0.1 mM – 1.4 mM	Saliva Sweat	(Azeredo, <i>et al.</i> , 2020)
PDA@NPGF	i-t	H ₂ O ₂	Alzheimer's disease.	2.53 μ A / μ M cm ² 1.00 μ A / μ M cm ²	-	0.1 μ M 0.27 μ M	1 μ M –100 μ M	-	(Sukeri, <i>et al.</i> , 2020)
Co@MOF-808/FTO	i-t	H ₂ O ₂	Alzheimer's disease.	382.27 μ A /mM cm ²	K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , Zn ²⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , NO ₂ ⁻ , CO ₃ ²⁻ , Cl ⁻	1.3 μ M	1 μ M –500 μ M	-	(Chang, <i>et al.</i> , 2020)
Pt Electrode Biosensor Arrays	i-t	Glutamate	Alzheimer disease,	170–200 nA/mM	-	1 μ M	0.005 mM – 0.7 mM	Blood Serum	(Kucherenko, <i>et al.</i> , 2019)
		Choline		130–150 nA/mM		2 μ M	0.001 mM – 0.2 mM		
		Acetylcholine	Myasthenia,	100–12 nA/mM		3 μ M	0.01 mM –0.3 mM		
		Glucose	Disorders of	150–170 nA/mM		1 μ M	0.01 mM – 2 mM		
		Lactate	cholinergic neurotransmission	440–460 nA/mM		3 μ M	0.005 mM – 0.4 mM		
Au@Fe ₃ O ₄ /GCE	i-t	Pyruvate DA	Neurological disorders	35–40 nA/mM 0.120 μ A/ μ M	NO ₃ ⁻ , CO ₂ ³⁻ , SO ₄ ²⁻ , Cl ⁻ , Cu ²⁺ , Zn ²⁺ , Al ³⁺ , Fe ³⁺ , Mg ²⁺ , Ca ²⁺ , K ⁺ , Na ⁺ , Serotonin, Histamine, β -endorphin, Trypramine, Acetylcholine, Phenethylamine, Caffeic acid, AA, UA	5 μ M 2.7 nM	0.01 mM – 2.5 mM 0 - 0.8 μ M	Blood Serum	(Thamilselvan, <i>et al.</i> , 2019)

GO – Graphene Oxide, ITO – Indium Tin Oxide, FTO - Fluorine doped Tin Oxide, PGE – Pencil Graphite Electrode, UA – Uric Acid, DA – Dopamine, AA - Ascorbic Acid, HE4 - Human Epididymis Protein 4, HAS – Human Serum Albumin, BSA – Bovine Serum Albumin, HQ - Hydroquinone, CC - Catechol, EP – Epinephrine, NEP – Norepinephrine, SPCE – Screen Printed Carbon Electrode, GC – Glassy Carbon Electrode, GE- Gold Electrode.

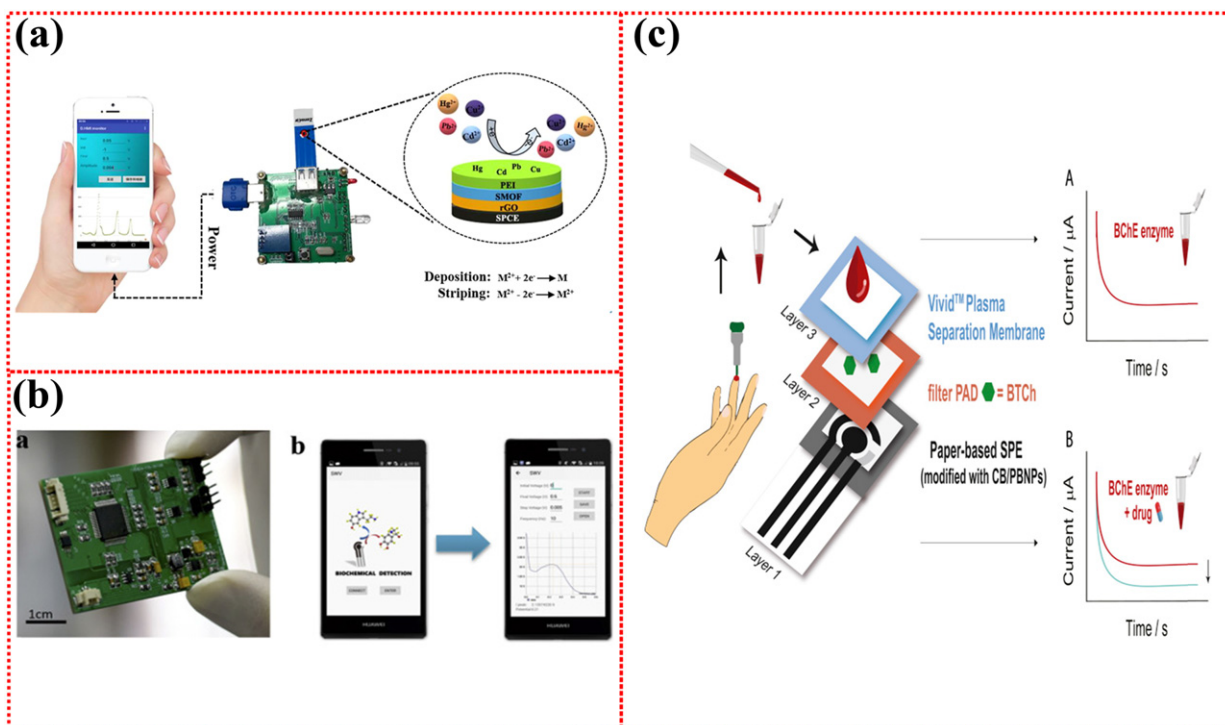


Fig. 3 (a) Schematic representation of the quantitative POCT system and the simultaneous detection of multiple metal ions by the rGO/SMOF/PEI modified SPCEs. The smartphone-based SWV system. (b) The image of SWV detector (a) and the welcome interface and real-time SWV detection on the smartphone screen. (c) Configuration of the origami paper-based device and schematic representation of the principle of detection. Reprinted with permission from (a) Xu, Z., *et al.*, 2020. A smartphone-based quantitative point-of-care testing (POCT) system for simultaneous detection of multiple heavy metal ions. *Chemical Engineering Journal* 394, 124966. (b) Ji, D., *et al.*, 2020. Smartphone-based square wave voltammetry system with screen-printed graphene electrodes for norepinephrine detection. *Smart Materials in Medicine* 1, 1–9 (d) Configuration of the origami paper-based device and schematic representation of the principle of detection. (d) Caratelli, V., *et al.*, 2020. Precision medicine in Alzheimer's disease: An origami paper-based electrochemical device for cholinesterase inhibitors. *Biosensors and Bioelectronics* 165, 112411.

~ 0.49 V (vs Ag=AgCl) and ~ 0.30 V (vs Ag=AgCl) for Cd^{2+} - Pb^{2+} , Pb^{2+} - Cu^{2+} and Cu^{2+} - Hg^{2+} , respectively. The sensor was reported with a low LOD of 1.5 nM, 4 nM, 1.6 nM and 0.5 nM for Hg^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} , respectively. Additionally, the sensor exhibited a successful detection of HMLs simultaneously in human blood serum samples with excellent recovery percentages (Durai and Badhulika, 2020a,b). Similarly, the trace level detection of Arsenic (As^{3+}) in the blood serum sample was reported using a specially modified SPCE with bismuth vanadate ($BiVO_4$) nanoflakes followed by the electrodeposition of polyaniline (PANI) ($PANI@BiVO_4/SPCE$). The as-fabricated modified electrode sensor exhibited a LOD of 0.0072 ppb with a linear range of detection from 0.01 to 300 ppb. The efficacy exhibited by these sensors in terms of selectivity, stability, and reproducibility proved that the perovskite material-based modified electrode sensors as a promising platform for ion-selective sensing in point of care and clinical diagnosis of heavy metal ion poisoning leading to different kinds of chronic and neural diseases (Durai and Badhulika, 2020a,b).

Smartphone-based electrochemical biosensors

The field of electrochemical sensing has provided a promising low-cost, rapid, sensitive, and selective platform for biomarker or analyte sensing in biological fluids. Though it is comparatively facile and portable than the conventional techniques, it has not been suitable for point of care diagnosis where the analysis can only be performed in a laboratory environment. To overcome the disadvantage of portability and make the analysis more user-friendly various techniques have evolved in the past decades with the help of microcontroller/ electronic circuits connected with a smartphone interface. This evolution of the electrochemical device miniaturization has gathered a significant reach interest in biosensing applications for point of care diagnosis of deadly diseases.

Xu *et al.* reported an adaptable and cost-effective point-of-care testing (POCT) platform for simultaneous determination of multiple analytes on-site. This POCT was inherited with a customized SPCE electrode modified using rGO, MOF, and PEI as shown in Fig. 3(a) (Xu *et al.*, 2020). The modified electrode sensor was connected to the quantitative PCOT system consisting of Cortex-M3 core-based ALIENTEK (STM32), a 32-bit microcontroller unit (MCU), and a 12-bit digital-to-analog converter (DAC) module. The major challenge to be addressed by the POCT was the potentiostat module which can deliver output positive potential, but the reduction potential of some metal ions was found negative. To overcome this vital complication a reverser integrated chip, TP7600 module was introduced in the circuit to change the positive potential output to the required negative potential for metal ion sensing. The sensor showed excellent sensitivity and stability with a low LOD of 0.296 μ M, 0.055 μ M, 0.351 μ M, and 0.025 μ M for Cd^{2+} , Cu^{2+} , Hg^{2+} , and Pb^{2+} ions,

respectively. This new platform of the smartphone-based biosensor was also equipped with a specialized android application and an OTG cable to connect mobile with the MCUs. Though this sensor has been reported for the water samples this can also be a promising platform for various low-cost facile point of care diagnoses. Similarly, Ji *et al.* (2020) reported a smartphone-based potentiometric biosensor for the detection of norepinephrine in biological fluids. This biosensor was reported with a simple square wave voltammetry technique employed on a screen-printed graphene electrode (SPGE). The Graphene ink was printed on the soft substrate to construct a flexible screen-printed graphene electrode. The detector was used to generate electrochemical excitation signals, monitor the resultant currents on the sensors, convert the current into digital code, and send them to a smartphone as shown in Fig. 3(b). The smartphone was reported as the core system with control over data processing and results in the display. The sensor exhibited a low LOD of 0.265 μM with an outstanding selectivity towards norepinephrine. These reports on the smartphone-based electrochemical sensor for neurotransmitter with an excellent LOD and selectivity proves it as an ideal platform for futuristic point of care diagnosing and wearable detectors.

Paper-based electrochemical biosensor

Paper-based electrochemical biosensors are the replica of conventional electrochemical sensors on the paper-based substrate via different fabrication techniques for biosensing applications. These are the low-cost, flexible biosensing platforms hydrophilic in nature in which the porosity of the substrate facilitates different fabrication techniques like chemical and physical modification with outstanding process controls. Recently, Caratelli *et al.* (2020) reported an origami paper-based electrochemical device for the detection of cholinesterase inhibitors such as physostigmine (PG), rivastigmine (RG), and donepezil (DP) in human blood samples using the amperometric technique. Fig. 3(c) depicts the construction of the origami paper-based device and a schematic representation of its detection principle. This paper-based electrochemical sensor was reported as a lab-on-a-chip technology to deliver a cost-effective and easy way to use sensing tool for personalized supervision of drugs for Alzheimer's disease. The sensor was reported with a linear range of detection from 0.01 to 0.5 μM ; 0.5–25 μM ; 0.5–30 μM towards PG, RG, and DP, respectively. The LODs were reported as 0.009 μM (PG); 0.4 μM (RG) and 1 μM (DP) for PG, RG, and DP, respectively. Thereby the low LOD with excellent sensitivity and selectivity proved the efficacy of the paper-based origami sensors as an effective low-cost platform for point of diagnosis.

Spectral Biosensors

The spectral biosensor (optical biosensor) is a compact analytical device comprising a biorecognition sensing element integrated with an optical transducer system. There is a wide variety of spectral biosensors reported for bioanalytical applications with underlying principles of operation such as Fluorescence detection, Surface-enhanced Raman spectroscopy (SERS), Surface Plasmon Resonance (SPR), Colorimetric, and Electrochemiluminescence detection. In this part of the article, we discuss more the advancement in the different spectral techniques toward ultra-selective and selective detection of neurological biomarkers in the biological samples and their successful applications in various clinical and point of care diagnosis.

Fluorescence detection

Fluorescence biosensors is a technique in which the activity of the biomolecules is quantified via an image with high spatial and temporal resolution Mathew *et al.* (2020) reported a simple cost effective "Turn-on" Fluorescence sensor for the determination of Xanthine in human biological fluids like human blood serum and urine. The sensor was fabricated using GSH capped copper nanoclusters (CuNCs) which were reported as the fluorescent probe for biosensing application. The reported mechanism of this sensor was attributed to the improved fluorescence effect due to the binding of XA on the surface of GSH CuNCs. The sensor exhibited excellent sensitivity and a short analysis time without a sample pre-treatment process. The sensor possessed a wide linear range of detection from 80 μM to 9 mM with a LOD of 6 μM .

Surface plasmon resonance and colorimetric

Surface plasmon resonance (SPR) biosensors work on the label-free optical biosensing technique in which the change in the refractive index due to the binding of biomolecules in the given sample is obtained as a read-out signal. Springer *et al.* (2020) reported the development of a surface plasmon resonance (SPR) based biosensor for the detection of complex protein biomarkers of Alzheimer's disease, namely protein tau and amyloid β (tau-A β). The sensor was fabricated using a new sandwich assay incorporating functionalized gold nanoparticles (AuNPs). The biosensor was reported successful in detecting the tau-A β complex in cerebrospinal fluid (CSF) with extremely high selectivity and low LOD of 1 pM. The colorimetric biosensors technique relies on the visible color change with respect to the concentration of the targeted analyte which can be used for quantitative measurements (Xia *et al.*, 2020). Xia *et al.* reported a hybrid dual-modal non-invasive biosensor for detection of exomes using a nature-inspired colorimetric and fluorescent technique. Although various techniques have been evolved for detection of exomes in the biological fluid the sensitive and accurate detection remains a vital challenge of the process. The reported biosensor was constructed using nature's "one-to-many" concept in which the biosensor would mimic the cactus with plentiful thorns to detect exosomes. The sensor was fabricated using the base of cholesterol-labeled DNA (DNA anchor) binding to streptavidin modified horseradish peroxidase (HRP) which is explained as the thorns of the cactus as shown in Fig. 4. Additionally, CD63 antibodies were introduced to modify the sensor which acted as the root to the cactus that captures exosomes, and the exosomes look like the stems. The sensor exhibited a wide linear range of detection from 1×10^4 to 5×10^5 particles/ μL with a LOD of 3.40×10^3 particles/ μL .

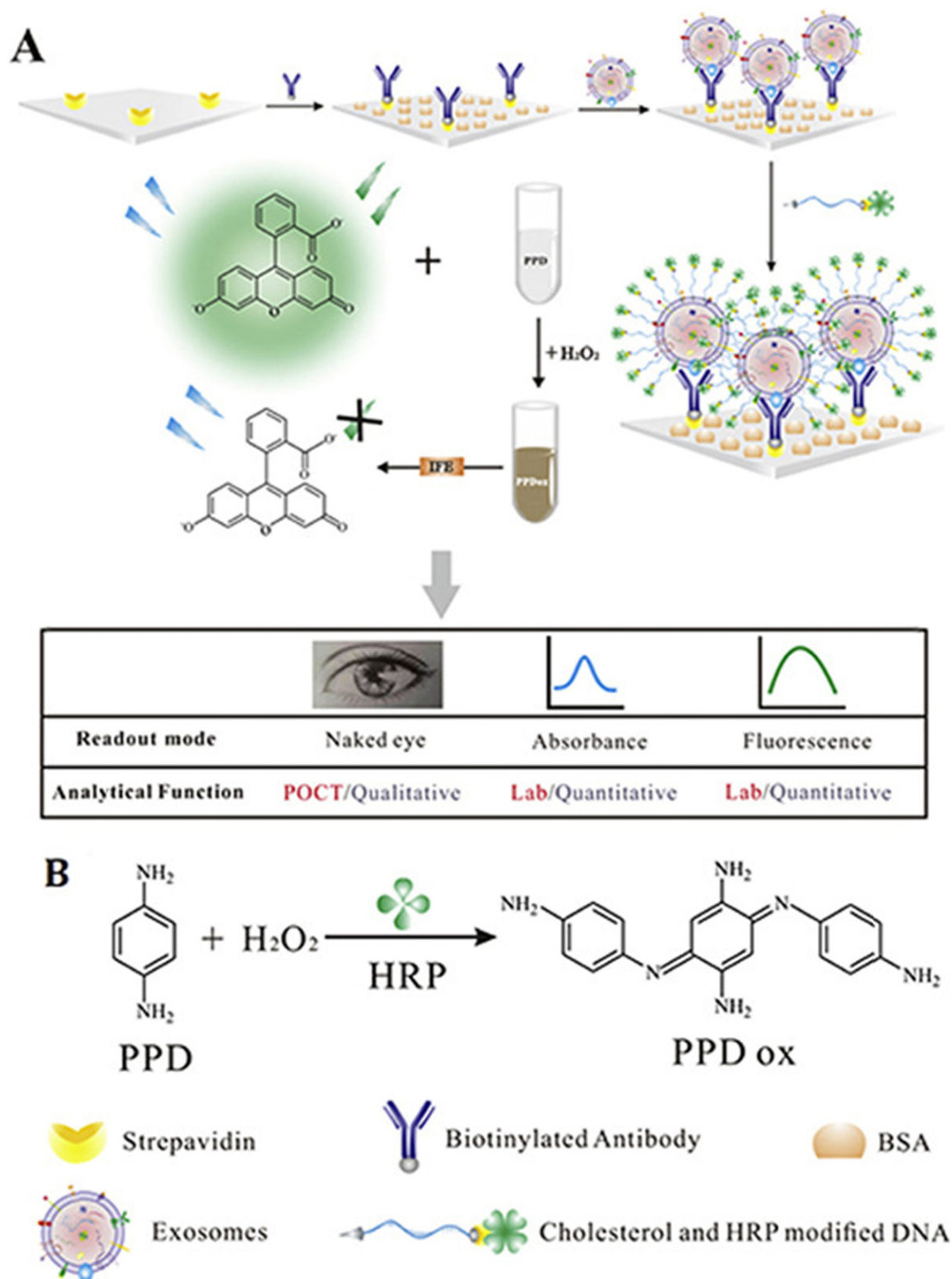


Fig. 4 (A) Working principle of the proposed method for exosomes detection, (B) Schematic representation of HRP-catalysed oxidation of PPD into PPDoX by H₂O₂. Reprinted with permission from Xia, Y., *et al.*, 2020. A nature-inspired colorimetric and fluorescent dual-modal biosensor for exosomes detection. *Talanta* 214, 120851.

and 3.12×10^3 particles/ μL employing colorimetric and fluorescent assays, respectively. The sensor also showed an excellent selectivity towards the exomes proving it as a promising platform for clinical diagnostic applications.

Electronic Biosensors

The electronic biosensors are the transducers, in which the interaction between the targeted biomolecules and the fabricated devices induces a significant change in the basic electrical values of the device such as resistance, inductance, or capacitance. In recent days, field-effect transistors (FET) devices have been exponentially used for biosensing applications. In this part, we would provide a clear insight into the advantages of the electronic biosensors over other conventional biosensors such as electrochemical and optical biosensors. The miniaturization process of an electrochemical biosensor would impact the reduction in the size of the reference electrode which in turn leads to degradation in the sensitivity and stability of the sensor due to the reduced active sensing area. To overcome the drawbacks and there has to be a significant advancement to achieve compact, lightweight-portable biosensors for wearable and point of care diagnosis. The concept of ion selectivity FET (ISFET) was first introduced in the year 1970 for the detection of biomolecules such as penicillin, DNA, proteins, enzymes, and cells (Kaisti, 2017). Herein, we debate more on the recent advancement in the field of electronic biosensors depending on three different conceptualizations such as FET, chemiresistive, and giant magnetoresistance to achieve a low-cost, rapid, selective, and sensitive detection of targeted biomolecules in the biological fluids.

Giant magneto resistance biosensors

The giant magnetoresistance effect (GMR) is the basic quantum mechanical magnetoresistance effect observed in multilayers composed of alternating ferromagnetic and non-magnetic conductive layers. Here, the changes in the local magnetic field due to the presence of biomolecules are transduced into equivalent electrical signals which are considered the readout signal. Under the spin-dependent scattering phenomenon of the GMR effect, the device's resistance is proportional to the magnetic field. The major advantages of the GMR biosensor over other types of biosensors are the high sensitivity, low cost, compatibility with IC technology, and suitability to assimilate with microfluidic devices. The merits reported for GMR biosensor can be attributed to the factors such as (1) non-magnetic clinical samples which cannot interfere with the readout signals of the biosensor due to its low intrinsic background signals. Thereby an enhanced sensitivity of the biosensors is achieved towards targeted biomolecules in biological fluids. (2) The GMR biosensors can be arrayed for multiplexed detection in a single assay without any need for optical scanning. (3) These GMR biosensors are reported to be insensitive to the sample matrix, allowing them to be used with a wide variety of samples with minimal sample preparation which makes them expedient for use in point-of-care diagnosis. (4) The GMR sensors can continuously quantify the local magnetic field changes enabling real-time monitoring of the bioassay, etc. Zhu *et al.* reported a GMR biosensor for the detection of exomes in biological fluids. Here, the sensor was fabricated via 2D MoS_2 - Fe_3O_4 nanostructures (MOFE) as magnetic responsive probes for signal amplification. Later, the as-synthesized MOFE was immobilized using an aptamer. The GMR biosensor was reported with a LOD of 100 exosomes (Zhu *et al.*, 2019). Additionally, the excellent sensitivity, stability, and reproducibility of the reported GMR biosensor for exomes proved it as a promising platform for a wide variety of biopsy and point of care diagnostic applications.

Other Types of Biosensors

Apart from the electrochemical, electronics, and spectral biosensors, there are other types of biosensors reported for facile, low-cost, and rapid detection of neurological biomarkers in biofluids. In this part, we discuss the recent reports depending on special working principles such as piezoelectric, cantilevers, etc. This discussion would provide a clear insight into the new emerging platform for facile detection of biomarkers enhancing the ability of low-cost, point of care, and wearable diagnostic applications.

Cantilever based biosensor

Cantilever or microcantilever biosensors are the new class of biosensors in which the stress induced in the cantilever surface due to the biomolecules is directly transduced into its mechanical deflection with high precisions. Taniguchi *et al.* (2020) reported a label-free, chronological microcantilever-based biosensor for ultra-selective detection of the Amyloid β Protein ($\text{A}\beta\text{P}$) in Serum. The $\text{A}\beta\text{P}$ is the vital biomolecule of amyloid plaques found in the brain of people with Alzheimer's disease. The microcantilever-based trace level $\text{A}\beta\text{P}$ biosensor was fabricated via immobilization of liposomes of various phospholipids such as 1,2-dipalmitoyl-sn-glycerol-3-phosphocholine (DPPC), DPPC/phosphatidylethanolamine (PE) and 1,2-dipalmitoyl-sn-glycerol-3-phosphorylglycerol (DPPG). The liposome was immobilized on the NiCr Strain gauge cantilever of the sensor on a silicon on insulator (SOI) wafer. The fabrication process was performed via microelectromechanical systems (MEMS), while a polydimethylsiloxane (PDMS) droplet-sealing structure was also applied to the cantilever of the biosensor. Hence, the enhanced selectivity of the sensor was attributed to the effect of cholesterol in addition to the phospholipid. The sensing ability of the biosensor was attributed to the charged hydrophilic group in the DPPG liposome which extended an electrostatic interaction towards the targeted $\text{A}\beta\text{P}$ which induces stress in the cantilever. This stress on the cantilever is observed as the sensing ability of the reported microcantilever biosensor. The sensor exhibited a LOD of 100 pM for human serum samples. This reported microcantilever biosensor gives a clear insight into the MEMS-based biosensing platform for clinical and point of care diagnosis.

Future Directions

The future scope in the field of biosensors is anticipated to rely on the development of highly stable, sensitive, and selective detection of complex biomarkers for the early diagnosis of neurological disorders in humans. The overall advancement expected in the field of biomarkers shortly can be towards: (1) A portable, laboratory-free, and user-friendly biosensing platform integrated into smart-phones applications for detection of complex biomarkers in various biological fluids, (2) Development in various active functional materials for microfluidic devices for in-vivo and in-vitro diagnosis and therapeutics, (3) Depending on versatile properties of special structured materials, an exponential development in the efficiency of biomarker detection is expected using new electrochemical sensing techniques such as photoelectrochemical analysis, sono-electrochemical analysis microwave activated electrochemical analysis, etc., (4) The other biosensor technologies like FET, GMR, Cantilever based biosensors could provide a wearable biosensing platform for early disease diagnosis and onsite health monitoring facility, and (5) Provided with miniaturization of these biosensing platforms, it could be integrated with a micro-electromechanical system (MEMS) for a novel drug delivery application.

Conclusion

In summary, this article provides a comprehensive insight into the variety of biomarkers and their detection techniques for the early diagnosis of neurological disorders in human beings. Biomarkers are the biological constituents of the body fluids which can indicate the normal and abnormal processes of a biological system. The detection of an abnormal concentration of targeted biomolecules in the body fluids is associated with various diseases and disorders. In this regard, most recent pertinent articles on different biosensor technology such as electrochemical, spectral, electronic, piezoelectric, cantilever-based biosensors and their analytical performance with efficacy towards an early clinical diagnosis of neurological disorders were assessed. In short, every biosensing technique has its advantage and disadvantages in the detection of targeted biomolecules. However, recent research has progressed through simultaneous biomarker detection techniques for effective and low-cost clinical diagnosis of different diseases. On the other hand, the miniaturization process of the biosensors provided with the application of novel nanostructured materials has paved a new avenue of research for wearable and user-friendly point-of-care diagnosis. Also, we believe that this broad insight into different biosensor technologies and their application would encourage more research into the field of biosensing. The major existing challenges and limitations of the biosensor technologies for early diagnosis of neurological disorders are the selection of the biomarker. Multiple biomolecules are existing in the biological fluids that can be considered biomarkers for the early diagnosis of neurological disorders.

Despite the availability of a wide spectrum of biomarkers, the identification of suitable biomarkers for the relevant application of diagnosis is of the highest priority. Firstly, the low physiological concentration of various neurotransmitters biomarkers demands an ultra-sensitive detection technique. Secondly, the presence of these biomarkers in the biological fluids discloses the presence of other biomolecules and cell tissues in the complex. This demands a selective biosensor that is active toward the targeted analyte and inactive to other biomolecules. Thereby, a highly selective biosensor is required for clinical sample analysis. Thirdly, stability and reusability are the two vital parameters for any biosensors defining the efficacy of the sensor. These parameters should be improved when compared to the current progress status of the reported biosensor. This can be achieved through the application of various highly stable perovskite materials with unique nanostructures and properties. The cost-effective development of the biosensing technology is highly crucial for the commercialization of biosensors and related early diagnosis applications. In this aspect, the smartphone-based electrochemical biosensors and the electronic FET-based biosensors have achieved a low-cost fabrication procedure with high-performance efficacy than the other biosensors discussed above. Thereby, these techniques pave a new path toward futuristic advancements in biosensor technology and applications. Finally, the miniaturization of the biosensors for the evolution of handy and wearable point-of-care diagnostic devices remains a vital challenge for the early diagnosis of neurological disorders.

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MEMS-Based Flexible Sensors

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Abstract

Micro-Electro-Mechanical Systems are predominantly fabricated on rigid substrates such as Silicon, Quartz, Glass, etc. However, a wide range of devices such as tactile, flow, wearable, and implantable sensors should be flexible. Therefore, such sensors should be fabricated on flexible substrates or smaller silicon substrates that are interconnected using flexible cables. The design, fabrication, and characterization of such sensors are different from that of conventional sensors made with rigid substrates. This chapter overviews the standard practices and protocols followed in fabricating flexible sensors. The most important mechanisms that govern the working of flexible tactile sensors are described, citing a few examples at relevant locations. This chapter also showcases some of the flexible sensors that have the potential to be used in real-time applications.

Key Points

- Introduce the relevance of flexible sensors.
- Provide an overview of the key considerations in fabricating flexible sensors.
- Discuss the key mechanisms governing the working of flexible sensors.
- Bring forth the most highlighted applications of flexible sensors.

Introduction

Flexible electronics, a technology that enabled the integration of sensors and transducers with arbitrarily curved surfaces and movable parts, led to the development of a wide variety of devices that helped humankind to improve the quality of living. MEMS-based sensors on flexible substrates are a natural evolution following the MEMS revolution and the advancement of flexible electronics. A variety of sensors such as accelerometers, microbolometers, pressure sensors, force sensors, temperature sensors, etc., have been developed on flexible substrates and demonstrated their utility in several applications. The application areas of flexible electronic devices include human health monitoring, wearable electronics, artificial intelligence, and robotics, among others.

Flexible sensor fabrication necessitates novel approaches in the design of active materials and conductors and the selection of the substrate material. In cases where bulk materials are to be used as substrate materials, they should either be thinned down to a deformable state or should be diced as micro-islands and connected using flexible interconnects. Micro Electro Mechanical System (MEMS)-based sensors are mostly implemented on semiconductor substrates such as silicon. Such semiconductor materials are brittle and therefore they can not withstand large deformation. Therefore, various polymer-based materials are used as the substrate material for flexible sensors.

This chapter comprehends the general considerations for the fabrication of flexible sensors, and flexible sensors that work on four cardinal transduction mechanisms, viz, capacitive, electrochemical, piezoelectric, and piezoresistive. A brief explanation of the physics of each of these mechanisms is included, followed by the most highlighted demonstrations of flexible sensors in each category.

Key Considerations for the Fabrication of Flexible Sensors

The choice of the substrate material and the conducting element are two critical considerations for a MEMS-based flexible sensor. The congruence of the substrate in fabricating a flexible sensor is decided by the degree of foldability, stretchability, and bendability. Polymeric materials such as Polyethylene Terephthalate (PET), Polyimide (PI), Polydimethylsiloxane (PDMS), Polyethylene naphthalate (PEN), Polyvinyl Alcohol (PVA), Polyurethane (PU), etc. are used as substrates for flexible sensors. These polymers have high degrees of stretchability, low Young's modulus, high chemical resistance, and transparency, making them suitable for fabricating flexible sensors. The selection of substrate for a specific sensor is based on the sensor fabrication process flow and ambient conditions in which the sensor is to be deployed. Most flexible substrates are sensitive to temperature and therefore low-temperature processes should be used to fabricate flexible sensors.

Metallization is an inevitable process step in the fabrication of sensors. In the conventional microfabrication process, Physical Vapor Deposition (PVD) techniques such as sputtering, thermal evaporation, and electron beam evaporation are used to create metal interconnects and contacts. Sputtering involves the generation of high-density plasma, whereas evaporation techniques are inherently high-temperature processes. Though plasma at low density for a short period of time could increase the adhesion of

metal on the flexible substrate, high-density plasma can etch most of the flexible substrates, and therefore, sputtering is not preferred for metallization on flexible substrates. Evaporation over a long duration can heat up the substrate leading to its expansion and similar undesired deformations. When the evaporation chamber is bigger, this effect can be minimized. Nevertheless, evaporation is also not recommended for metallization on flexible substrates. Both these techniques yield metal thin films having thicknesses of the order of a few hundred nanometers. When used in flexible applications, thin metal films can develop cracks leading to a discontinuity in interconnects. To mitigate the issues with these metallization techniques, processes such as electroplating, screen printing, etc. are used to make electrodes on flexible substrates. Electroplating uses electrical current to form a metal coating on the substrate with the help of reduced metal cations. A thin metal layer deposited on the substrate using sputtering or evaporation acts as the seed layer for the growth of electrodeposited metal. The thickness of the electrodeposited metal could be from a few hundred nanometers to a few ten micrometers. Screen printing uses conductive metal inks to form metal patterns on the substrate. Metal particles or conductive particles like graphene powder are dispersed in a binder medium to prepare the conductive ink. Stencils having the pattern of electrodes are used to make electrodes on the flexible substrate. After applying the conductive ink, the substrate is heated at a moderate temperature to cure the ink.

Conventional wafer-level packaging techniques used for rigid substrates can not be employed in the packaging of flexible sensors. Laser-assisted packaging is one of the techniques used to package MEMS flexible sensors. Laser beams can be employed for the dicing and singulation of flexible substrates. Laser beams have high power density, small spot size, and faster operation that helps achieve high-precision dicing with minimal kerf losses in the merest possible time. Unlike conventional dicing methods, laser dicing is a dehydrated process, that eliminates the possibility of exposing the substrate to liquids during the dicing process. Since laser beams can be guided using a computer program, irregularly shaped structures can be diced out of the larger substrate, which is a key consideration for flexible MEMS sensors to be used in wearable and implantable applications. Laser dicing processes could be categorized into ablation-based dicing, and stealth dicing, depending on the underlying mechanism. Ablation-based dicing relies on the absorption of the pulsed laser energy incident on the substrate, which induces crystallographic deformations on the laser focusing point. This method may locally raise the temperature of the substrate. Stealth dicing employs laser beams having wavelengths that are capable of transmitting through the substrate. Pulsed laser sources having narrow pulse widths and high repetition rates are used in this dicing method, which can induce sub-surface defects, which can propagate as cracks.

Creating electric connections from flexible substrates to the contact pads on the packaging is a challenging task. Unless carefully engineered, conventional wire bonding techniques can not be used to bring out connections from flexible substrates. Laser soldering can be successfully used in such applications where customizable point-specific soldering is required. Laser soldering offers a small spot size for high-precision soldering on micron-level contact pads on MEMS flexible sensors. In this process, the filler material is heated to its softening temperature, which is close to 450 °C to establish a connection to the substrate. Since the heating process is non-contact and localized, the temperature rise will not affect the devices on the substrate.

Classification of Flexible MEMS Sensors Based on Their Working Principle

Capacitive Flexible Sensors

Capacitive flexible sensors are fabricated as parallel plate capacitors or inter-digitated electrode (IDE) structures. The capacitance of a parallel plate capacitor is given by:

$$C = \epsilon A / d$$

Where “ ϵ ” is the dielectric constant, “ A ” is the overlapping area of the electrodes of the capacitor, and “ d ” is the distance between the plates of the capacitor. Ideally, changing any of “ ϵ ”, “ A ”, and “ d ” can lead to a change in capacitance. Therefore, capacitive sensors can be categorized into three: variable dielectric, variable area, and variable pole distance.

Capacitive sensors have a simple device structure, low detection limit, wide application range, fast dynamic response, and low power consumption, enabling them to be used in a wide variety of applications. The dielectric material of the capacitor is least affected by the variation in humidity and temperature. Also, in cases where a conductor of a low-temperature coefficient is used, the thermal expansivity is minimal. Therefore, capacitive sensors are the least sensitive to changes in temperature.

Stretchable strain sensors can be better attached to uneven surfaces like human skin. Such sensors should be able to adhere to nonflat surfaces that have finer topology to facilitate real-time signal transduction. Stretchable sensors must maintain their functionality even in their stretched state. These sensors are made to measure high strain levels, typically more than 50%. When stretched in the longitudinal direction, the width and thickness of the capacitive sensor may reduce. The linear mechanisms of this stress are given by:

$$\frac{\Delta l}{l} = \epsilon_x \quad (1)$$

$$\epsilon_y = \epsilon_z = -\nu \epsilon_x \quad (2)$$

$$l_{stretch} = l(1 + \epsilon_x) \quad (3)$$

$$w_{stretch} = w(1 - \nu \epsilon_x) \quad (4)$$

$$d_{stretch} = d(1 - \nu \epsilon_x) \quad (5)$$

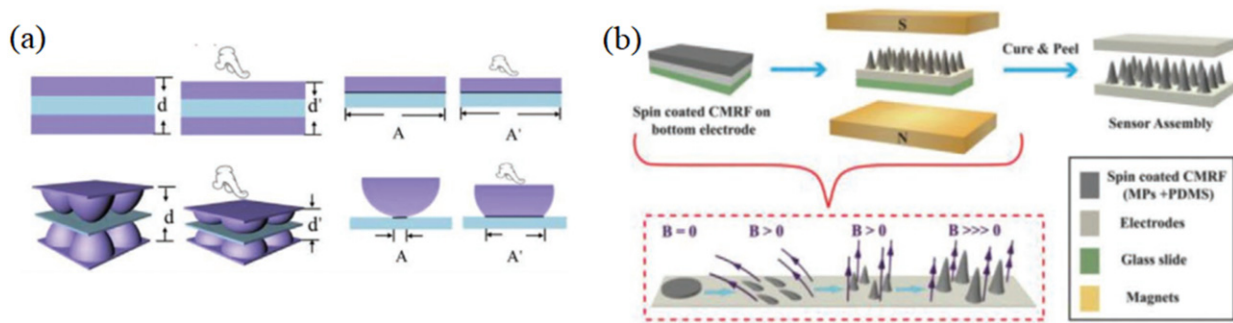


Fig. 1 (a) Pressure sensors with dome-shaped dielectric layer, and (b) that with micro-needle shaped dielectric material. Reproduced from (a) Xiong, Y., Shen, Y., Tian, L., *et al.*, 2020. A flexible, ultra-highly sensitive and stable capacitive pressure sensor with convex microarrays for motion and health monitoring. *Nano Energy* 70, 104436. (b) Asghar, W., Li, F., Zhou, Y., *et al.*, 2020. Piezocapacitive flexible E-skin pressure sensors having magnetically grown microstructures. *Advanced Materials Technologies* 5 (2), 1900934.

Substituting in the equation for capacitance,

$$C_{stretch} = C_0(1 + \varepsilon_x) \quad (6)$$

Where, l , w , and d represents the length, width, and thickness of the sensor respectively and ε_x , ε_y , and ε_z indicate the strains applied on x , y , and z axis respectively. This indicates that the capacitance of the device, when stretched, is a function of the strain in the x -direction only.

The stretchability of the electrode is another important parameter for flexible strain sensors. Efforts to improve the stretchability of the strain sensor electrode are underway, where the geometric modification of the electrode surface is one of the key considerations in this regard. Even though a strong adhesion between the flexible substrate and the electrode material is established, electrodes can break when the sensor is subjected to high deformation. Some topological innovations to improve the reliability of the electrode structures are serpentine structure, mesh structure, woven structure, buckling structure, etc.

Capacitive flexible sensors can be fabricated with a microstructured or patterned dielectric layer to increase sensitivity. The most common microstructural modifications on the dielectric layer are micro-pyramid structure, micro-dome structure, micro-pillars, micro-porous structure, etc. Xiong *et al.* (2020) fabricated a PDMS-based micro-dome structure that can withstand large deformation in both thickness and area directions. A schematic illustration of the micro-dome structure is given in Fig. 1(a). Asghar *et al.* (2020) developed a flexible micro-needle-based flexible pressure sensor using a magnetically grown dielectric interface. This technology is mold-free and large-area compatible and is schematically shown in Fig. 1(b).

Table 1 compares five common microstructural modifications on the dielectric material and their influence on the performance of the capacitive sensors.

Electrochemical Flexible Sensors

Electrochemical sensors work on two-electrode or three-electrode configurations to effectuate the sensing phenomena. A two-electrode system consists of a working or sensing electrode where the chemistry of interest occurs, and a counter electrode that completes the electrochemical system by acting as the second half of the electrochemical cell. A fixed potential is applied across the two electrodes and the resulting current is measured at either of the electrodes. The counter electrode maintains a constant potential while allowing current to flow through the cell. When used in electrochemical sensors, the current flow through the electrochemical cell will change, resulting in a change in potential across the cell. To mitigate this issue, a third electrode, known as the reference electrode is added to the electrochemical cell to make it a three-electrode system. In such systems, the potential difference between the working and reference electrodes is kept constant and the counter electrode passes all current that is required to stabilize the system.

Flexible electrochemical sensors utilize electrochemical reactions to tackle biomolecular interactions in humans. Along with flexibility, such sensors should be lightweight, stable long-term, and sensitive to electroanalytical parameters of interest. The most important electrochemical sensing methods are briefly described below:

Flexible potentiometric sensors

Potentiometric sensing is generally accomplished using two-electrode systems. The open circuit potential (OCP) in such sensors is between the sensing electrode and the counter electrode. Such sensors are also termed ion-selective sensors. The sensing electrode is modified with an element that can selectively detect the analyte of interest. When the analyte binds with the material coated on the sensing electrode, its potential will change, whereas the counter electrode will maintain constant potential. The Nernstian equation governs the change in OCP. For flexible electrochemical sensors, the ion-selective electrode must be in solid form. The typical formulation of an ion-selective electrode is a polymer matrix having an ionophore dispersed in it, whereas the reference electrode is Ag/AgCl coated with a polymer saturated with Cl ions to maintain a constant potential. The ion-selective material

Table 1 Comparison of different microstructured dielectric materials used in capacitive sensors

Type	Schematic	Advantages	Disadvantages	Summary	Challenge
Micropyramid		First proposed The best performance	Small linear range	Uniform Controllable Expensive Complex	1) Nonlinear at high pressure 2) Unstable nonstationary contact 3) Small capacitance/easily affected 4) Device thickened or opaque
Microdome		Distinguish between different forces	Greater viscosity Less deformability		
Microneedle/pillar		Larger deformation Distinguish different forces	Viscoelasticity High loss		
Microporous		Light mass Low hysteresis Fast response speed High compressibility	Uneven hole size and distribution	Uneven Uncontrolled Low-cost Simple	
Natural plant-based		Simple Green Low cost Easy to get	Difficult to standardize production		

Note: Qin, J., Yin, L.-J., Hao, Y.-N., *et al.*, 2021. Flexible and stretchable capacitive sensors with different microstructures. *Advanced Materials* 33 (34), 2008267.

should have excellent adhesion with the conductive material of the sensing electrode and the same should be highly selective to the other constituents in the analyte. Lee *et al.* (2017) fabricated a sensor with a porous structure to monitor parameters in sweat using potentiometric sensors. The schematic of the sensor is shown in Fig. 2.

Flexible voltammetric sensors

Voltammetric techniques such as linear sweep voltammetry (LSV), cyclic voltammetry (CV), and pulse voltammetry have been widely used in flexible electrochemical sensors. Such sensors are three-electrode systems in which a time-dependent voltage is applied to the reference electrode and the current flowing through the counter electrode is measured. When a voltage lower than the redox potential is applied to the system, reduction of the electroactive species takes place at the electrode-analyte interface, whereas a voltage higher than the redox potential leads to the oxidation of the electroactive species. Electroactive species can undergo oxidation or reduction at the electrode depending on the redox potential applied. The electrochemical behavior of the electroactive species on the electrode can be evaluated using LSV or CV. However, these techniques do not provide high sensitivity due to the background charge arising from the charging at the electrode. This can be mitigated using differential pulse voltammetry (DPV), where the background current is measured before the application of potential, and the current difference while applying the voltage is correlated with the concentration of the electroactive species. A wearable sweat sensor that works on DPV was developed by Tai *et al.* (2018) for the in-situ measurement of the drug methylxanthine (Fig. 3). This sensor works on three-electrode configuration with the necessary electronics integrated with it.

Flexible amperometric sensors

Amperometric sensors are three-electrode systems, wherein a constant voltage is applied between the sensing electrode and the reference electrode, and the resulting current is measured between the sensing and counter electrode. The working electrode is functionalized with the target recognition element. The current at the electrode is proportional to the redox reaction at the electrode-liquid interface, which is decided by the concentration of the target analyte. Amperometric sensing helps to analyze the time-dependency of the target molecule reaction. These sensors offer low detection limits, enabling them to use in flexible and wearable applications. Amperometric sensing is the working principle of most enzymatic sensors, where the enzymes for a particular reaction are attached to the working electrode, which will facilitate the chemical reaction with the target. A classic example of flexible amperometric sensors used in real-world applications is the sensing of metabolites in the human body.

Ion-selective field effect transistor (ISFET)

ISFETs are potentiometric devices, that evolved out of the conventional MOSFETs. A generic MOSFET will have three terminals; source, drain, and gate. As opposed to MOSFETs, the gate region of the ISFETs has ion-selective membranes or molecular receptors for the analyte of interest. The current through the ISFET channel is controlled by the charge developed by the gate material upon sensing the analyte molecule, which is analogous to the voltage applied to the gate terminal in the conventional MOSFET. Flexible

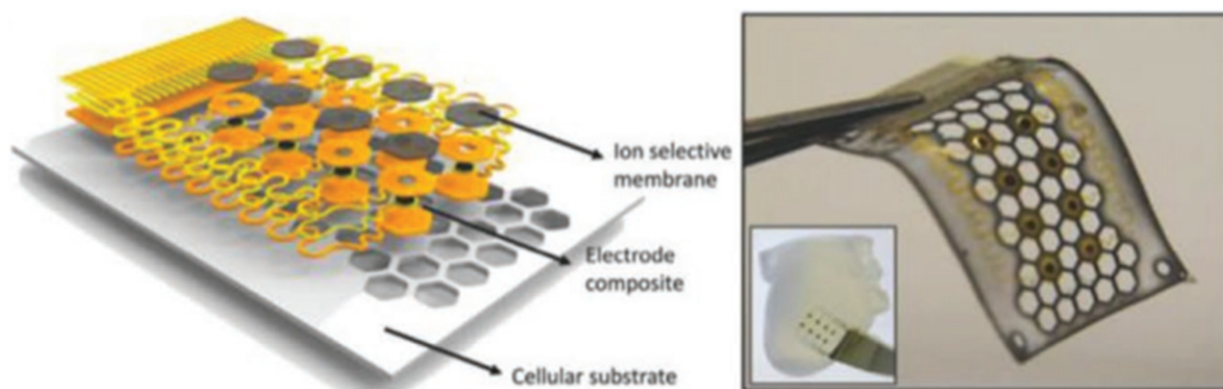


Fig. 2 Schematic representation of the porous sensor to detect parameters in sweat (left) and the photograph of the fabricated sensor (right). Reproduced from Lee, Y.K., Jang, K.I., Ma, Y., *et al.*, 2017. Chemical sensing systems that utilize soft electronics on thin elastomeric substrates with open cellular designs. *Advanced Functional Materials* 27 (9), 1605476.

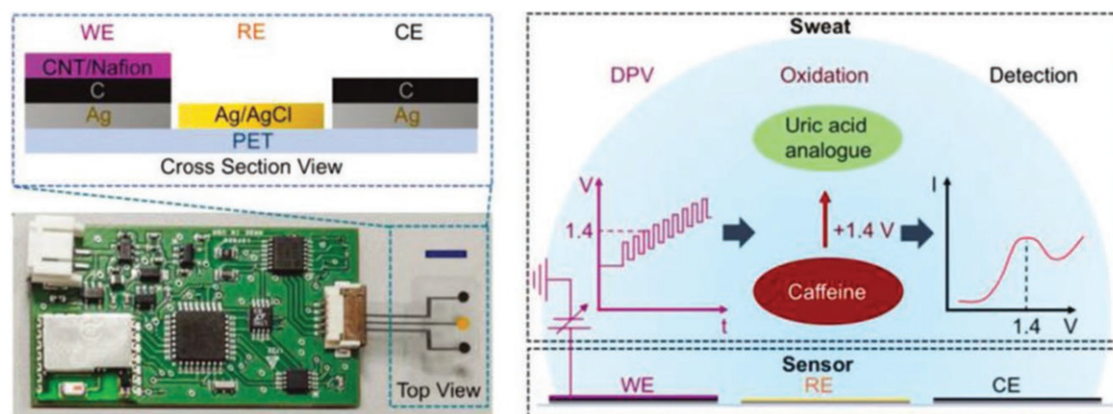


Fig. 3 Wearable sweat sensor that works on differential pulse voltammetry (DVP). Reproduced from Tai, L.-C., Wei, G., Minghan C., *et al.*, 2018. Methylxanthine drug monitoring with wearable sweat sensors. *Advanced Materials* 30 (23), 1707442.

ISFETs can be fabricated using organic or inorganic semiconductor materials. The gate material of the ISFET is chosen in such a way that it can facilitate the integration of the molecular receptors or ion-selective electrodes for a specific target analyte. As an example, CVD-deposited graphene functionalized with GOx was used for glucose sensing. Flexible ISFETs have also been used in the detection of electroactive analytes in biological samples such as dopamine, ascorbic acid, adrenaline, etc.

Piezoelectric Flexible Sensors

The ability of certain materials to generate electric charges in response to applied mechanical stress is termed the piezoelectric effect. Piezoelectric materials are dielectric in nature. When mechanical stress is applied to a piezoelectric material, charge develops across both faces of the material, resulting in a potential difference. The voltage developed across the piezoelectric material is proportional to the applied force, which is expressed by the piezoelectric coefficient. Most piezoelectric materials are ceramic materials and therefore they can not be used in flexible applications. A few demonstrations exist where the powder form of ceramic materials such as Lead Zirconate Titanate (PZT), Zinc Oxide (ZnO), etc. was dispersed in a polymer matrix to realize flexible piezoelectric materials. Such composite materials exhibit piezoelectric properties much lower than ceramic piezoelectric materials.

Polymer piezoelectric materials such as Polyvinylidene Fluoride (PVDF) and its co-polymer PVDF-Trifluoroethylene (PVDF-TrFE) are ideal materials for developing piezoelectric flexible sensors. PVDF is formed by polymerizing the monomer vinylidene fluoride, which is known to exhibit excellent piezoelectric properties. PVDF has four crystalline structures which are termed α , β , γ , and δ ; among them, β got the highest piezoelectric coefficient. The piezoelectric coefficient of PVDF can be enhanced by adding powder forms of PZT, ZnO, etc. [Tian *et al.* \(2019\)](#) prepared a PZT/PVDF composite through non-solvent-induced phase separation combined with high-pressure crystallization to yield a lamella structure that has superior piezoelectric performance. The lamella structure has an ultra-fast response (21 ms) and excellent sensitivity (6.38 mV/N) due to the inter-layer potential accumulation effect and rapid stress release in the structure. This is demonstrated by incorporating flexible sensors prepared using the lamella structure in a table tennis racket for personalized training.

Wearable and implantable devices require biocompatible piezoelectric materials. Piezoelectric biomaterials are being extensively used in fabricating implantable devices in the current decade, as their chemical and physical properties can be tuned by their changing microstructures, designing molecular structures, incorporating dopants, and fabricating heterogeneous structures. The piezoelectric properties of biomaterials depend on their phase, shape, and growth orientation. The most common bio-piezoelectric materials are collagen fibrils, silk, cellulose, chitosan, chitin, etc. Among all these materials, silk has been extensively studied in the present decade to fabricate biocompatible sensors and transducers. Silk fibroins extracted from silk cocoon exhibit moderate piezoelectric properties due to the presence of β -sheets (otherwise known as silk II form). Silk fibroins are transformed into solution form, which is then used to make thin films, nanofibers, etc. to be used in flexible sensors. Flexible tactile sensors, pressure sensors, piezoelectric micromachined ultrasonic transducers (PMUTs), etc. were developed using silk thin films.

Aligning piezoelectric domains is important to yield maximum piezoelectric response out of a piezoelectric polymer. Domain alignment in a piezo-ceramic is done through a process known as poling, in which a high electric field is applied across two faces of the material. In certain cases, piezoelectric polymers are also subjected to poling to align their domains. By virtue of the nature of piezoelectric thin film or fiber formation out of a piezoelectric polymer solution, in-situ poling takes place in the resulting polymer structure. Thin films of piezoelectric polymers are predominantly made using the spin-coating technique, where the solution to be spin coated is dropped at the center of the substrate and it is spun at a suitable speed to yield the desired thickness. The viscosity of the solution and the spin coating parameters such as speed, time, number of steps, etc. decides the thickness of the resulting film. During spin-coating, a stretching field arises in the spin-coated thin film from the center to the periphery, which will mechanically align piezoelectric domains in the thin film. Other thin-film formation techniques such as screen printing, and doctor blade coating does not provide a stretching field and therefore they will not facilitate the in-situ alignment of the piezoelectric domains. Electrospinning is the most common technique used to form piezoelectric nanofibers from their solutions. In electrospinning, a very high electric field is applied between the needle of the solution-loaded syringe and the substrate. When the piston of the syringe is pushed by a stepper motor-enabled mechanism with micro-scale precision, nanofibers will be formed from the needle and collected at the substrate. The high electric field applied in the electrospinning process induces in-situ poling in the nanofibers.

Piezoresistive Flexible Sensors

Piezoresistivity is an electromechanical phenomenon in which a reversible change in the electrical conductivity of a material occurs when subjected to mechanical strain. The change in resistance can be volumetric, superficial, or interfacial, among which the volumetric effect is the most significant. Piezoresistivity arises due to a reversible microstructural change in the material that results in a change in electrical continuity in the material. The applied strain impacts the band structure of the device, which affects the band-to-band conduction of electrons, resulting in an increase or decrease in the resistance of the material.

The resistance (R) of a homogeneous material is given by Ohm's law:

$$R = \frac{\rho L}{A}$$

Where, ρ is the electrical resistivity, L is the length of the material, and A is the cross-sectional area of the material. As it is evident from the equation, the resistance of a material is a function of the geometric parameters and material properties. Applied stress can induce changes in the geometry as well as the material properties, resulting in a change in the resistance of the material.

The gauge factor (GF) describes the piezoresistivity, which is defined as the change in resistance per unit strain. The GF of a piezoresistive material is given by the equation:

$$GF = \frac{\Delta R}{R \epsilon}$$

Where, $\frac{\Delta R}{R}$ is the fractional change in resistance with strain and ϵ is the strain. The change in resistance can be expressed as the sum of the change in resistance due to the geometric effects $(1 + 2\nu)\epsilon$, where ν is the Poisson's ratio of the material, and the change in resistance due to resistivity change $(\frac{\Delta \rho}{\rho})$.

Therefore,

$$GF = (1 + 2\nu) + \left(\frac{\Delta \rho}{\rho \epsilon} \right)$$

The electromechanical sensing response of piezoresistive materials is linear over a wide range of strains. The high sensitivity, linearity, and ease of fabrication make piezoresistive materials an ideal choice for practical applications.

Rigid and brittle inorganic materials such as metals, polycrystalline and single crystalline silicon, and nitride materials are predominantly used as piezoresistive materials. However, these materials are not ideal for flexible applications, as they require materials that are stretchable and conformal to the surface on which they are attached. Flexible piezoresistive materials are fabricated by incorporating conductive nanomaterials in the polymer matrix. The flexible nature of polymer materials along with the piezoresistive properties of conductive nanomaterials makes them ideal candidates to develop flexible and wearable sensors. Such material systems can be broadly classified into three categories: (a) conductive polymeric composite, (b) porous conductive material, and (c) architected conductive material. **Fig. 4.**

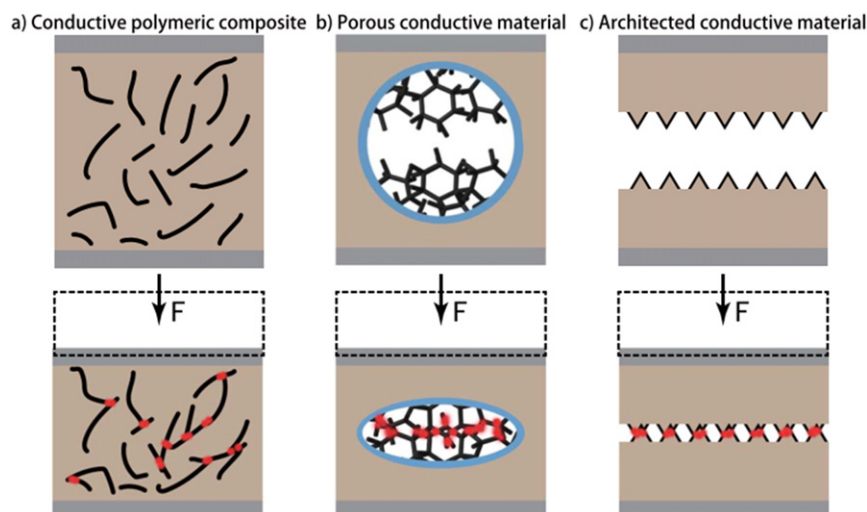


Fig. 4 Schematic representation of microstructures in (a) conductive polymeric composite, (b) porous conductive material, and (c) architected conductive material. Reproduced from Li, J., Fang, L., Sun, B., Li, X., Kang, S.H., 2020. Recent progress in flexible and stretchable piezoresistive sensors and their applications. *Journal of the Electrochemical Society*, 167 (3), p. 037561.

Conductive polymeric composite

Conductive polymeric composites consist of a conductive material dispersed in the polymer matrix. The conductive filler within the polymer matrix moves under the compressive force resulting in temporary conductive paths that result in a change in resistance. The most common conductive fillers include carbon nanotubes (CNTs), graphene, and other conductive materials such as metallic powders. CNTs are layered arrangement of cylindrical molecules of carbon atoms that has very high electrical conductivity and peculiar mechanical properties making them a perfect filler material for conductive polymeric composites. Graphene is a two-dimensional material having carbon atoms arranged in a hexagonal lattice structure. Graphene has excellent mechanical, electrical, and thermal properties, thereby making itself a suitable material to form conductive polymer composite. The most common metallic particles used to create conductive polymer composites are copper, zinc, aluminum, nickel, stainless steel, etc. Polymers such as PDMS, Ecoflex, PVDF, PU, etc. are used as polymer matrices to prepare conductive polymeric piezo composite with these materials. Filler material at the desired quantity is added to the polymer material in liquid form and stirred at room temperature or elevated temperature to prepare the polymer composite. This material is then formed into thin sheets of fiber by using standard film-forming or fiber-making practices.

Porous conductive material

Porous conductive materials have a three-dimensional porous structure in the conductive material. The porous matrix will compress and expand depending on the force applied, resulting in a change in resistance. Conductive foams have been widely used to prepare porous conductive materials. The three-dimensional interconnected structures provide the advantages of high flexibility, large surface area, and lightweight. Conductive foams can be categorized into four: conductive composite foams, monolithic conductive foams, porous fibers, and conductive material-coated foams. Conductive composite foams are prepared by combining conductive fillers and polymeric components. Such foams are usually prepared using the 'freeze-drying' or 'casting-etching' method. Monolithic conductive foams are 3D porous foams prepared using conductive materials such as graphene, and CNTs. These materials can be organized into porous structures in three-dimension, incorporating pores of various size shape, and morphology. Hence they offer the possibility of controlling electrical and mechanical properties leading to a wide range of applications. Porous fibers are three-dimensional structures having a fibrous structure that could offer stretchable and flexible properties. When these structures are loaded, the microstructures in the porous fiber come in contact with each other conductive pathways leading to piezoresistive properties. Electrospun conductive fibers, yarn-like conductive fibers, etc. are examples of such materials. In conductive material-coated foams, materials that have inherent porous structures are deposited with conductive materials through techniques such as sputtering, evaporation, dip-coating, wet-chemical deposition, etc. The dip-coating method is the preferred choice among these techniques because this technique is highly scalable.

Architected conductive material

Architected conductive materials have a custom-designed geometry. Microstructures in these materials encounter large changes in the contact area, resulting in a change in resistance. The material architecture is done in such a way that it amplifies the mechanical loading effects, leading to a resistance change that results in an increase in sensitivity. The material design could be nature-inspired, and periodical. In nature-inspired design, the delicate biological systems in living organisms, that sense mechanical signals are replicated in the material structure to enhance its strain sensitivity. As an example, the interlocked dermal-epidermal layers beneath human fingertips that help to recognize contact force were replicated by [Park et al. \(2014\)](#) using interlocked micro-dome arrays of PDMS-CNT composites. In this architecture, the area of the dome-dome contact point increases with increasing stress, which

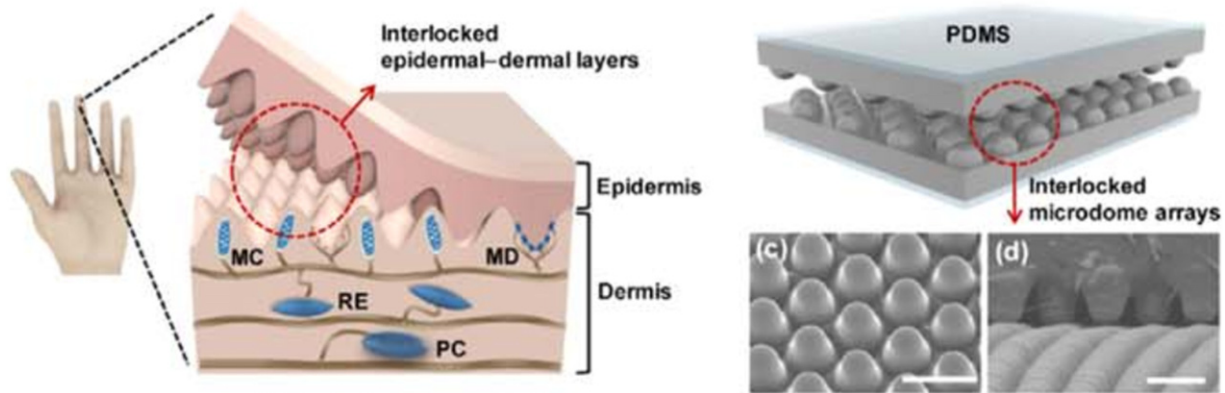


Fig. 5 Electronic skin using CNT-coated pyramidal layer-based tactile sensor for touch sensing. Reproduced from Chou, H.H., Nguyen, A., Chortos, A., *et al.*, 2015. A chameleon-inspired stretchable electronic skin with interactive colour changing controlled by tactile sensing. *Nature Communications* 6 (1), 1–10.

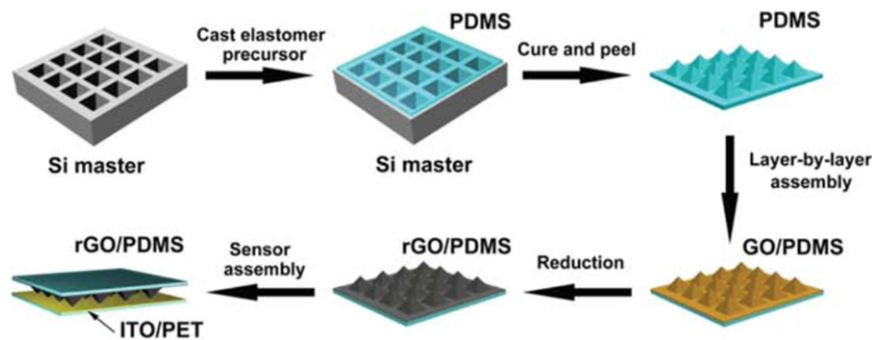


Fig. 6 Reduced graphene oxide/PDMS - based flexible tactile sensors. Reproduced from Zhu, B., Niu, Z., Wang, H., *et al.*, 2014. Microstructured graphene arrays for highly sensitive flexible tactile sensors. *Small* 10 (18), 3625–3631.

increases the tunneling current. Such devices exhibit a fast response time of 41 ms with high sensitivity. Researchers have demonstrated architectures inspired by the color-changing capabilities of chameleon and cephalopod skins. Chou *et al.* (2015) integrated piezoresistive and color-changing capabilities on electronic skin using a CNT-coated pyramidal layer and an electrochromic polymer that changes its color from dark red to pale blue with an increase in pressure (Fig. 5).

Periodic structures such as pyramids, pillars, domes, etc. have been employed in piezoresistive flexible tactile sensors. Zhu *et al.* (2014) fabricated a tactile sensor with pyramids made of reduced graphene oxide (rGO)/PDMS and flat ITO-coated PET film that exhibits exceptionally good sensitivity. The fabrication flow for the same is illustrated in figure. (Fig. 6).

Conclusion

This chapter presents a comprehensive overview of MEMS-based flexible sensors. An in-depth analysis of the important considerations in fabricating the flexible sensors, from the selection of the substrate material to the device packing is elaborated. The key guiding principles of the working of tactile sensors including capacitive, electrochemical, piezoelectric, and piezoresistive are discussed in detail with their physics and fabrication methods. Examples are provided in each of these sections to elucidate the design aspects and working principle.

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Flexible Strain and Pressure Sensors for Electronic Skin

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Abstract

Soft mechanical strain and pressure sensors are critical components of electronic skin (e-skin) and its wide-ranging applications including health monitoring, rehabilitation, robotics, Internet of Things (IoT) etc. This chapter reviews the state-of-the-art research related to the flexible and wearable pressure and strain sensors, particularly the ones developed using unconventional fabrication processes such as multi-material 3D printing and microfluidics. Various transduction mechanisms for pressure and strain sensing such as resistive, capacitive, piezoelectric etc. are discussed. Lastly, the challenges related to the integration, robustness and achieving energy autonomy for e-skin using these mechanical sensing technologies are presented.

Nomenclature

PDMS Polydimethylsiloxane
TENG Triboelectric nanogenerator
PENG Piezoelectric nanogenerator
PZT lead zirconium titanate
CNTs Carbon nanotubes
NC Nanocomposite
P(VDF-TrFE) Poly(vinylidene fluoride-co-trifluoroethylene)
1D, 2D, 3D One dimensional, Two dimensional, Three dimensional
 Q_T Transferred charges
 V_{oc} Open circuit voltage
HMI Human-Machine Interactions

Glossary

Biocompatibility The ability of a material to perform with an appropriate host response in a specific situation.
Electronic skin Artificial smart skin with multisensory devices and system and associated electronics that mimics the properties of human skin such as stretchability, self-healing, dexterity, power efficient computing etc.
Soft sensors Sensors that are mechanically flexible and/or stretchable.
Piezopotential Polarization from all the dipole units inside the piezoelectric material, results in a macroscopic potential drop between two electrodes.
Internet-of-Medical-Things (IoMT) Connected billions of wearable devices/sensors into a communication network allowing patient-doctor communications periodically or in real-time for digital healthcare.

Key Points

- Biomimicking pressure and strain sensors are critical for haptic sensing.
- Various transduction mechanisms for pressure and strain sensing are presented.
- Unconventional fabrication processes such as 3D printing and microfluidics are presented.
- Applications of soft pressure and strain sensors in robotics are discussed.

Introduction

Electronic skin (e-Skin) is the electronic interface that often mimics the morphology and functionalities of human skin (hereafter referred to as only 'skin') (Dahiya, 2019; Dahiya *et al.*, 2019; Herbert *et al.*, 2020; Ntagios *et al.*, 2020b; Ozioko *et al.*, 2021a; Wang *et al.*, 2015; Zumeit *et al.*, 2022; Ozioko and Dahiya, 2022; Ntagios and Dahiya, 2022; Neto *et al.*, 2022; Liu *et al.*, 2022b,a; Dahiya *et al.*, 2021). The e-Skin research has attracted considerable attention in recent years to provide sensory and/or haptic feedback in growing areas such as

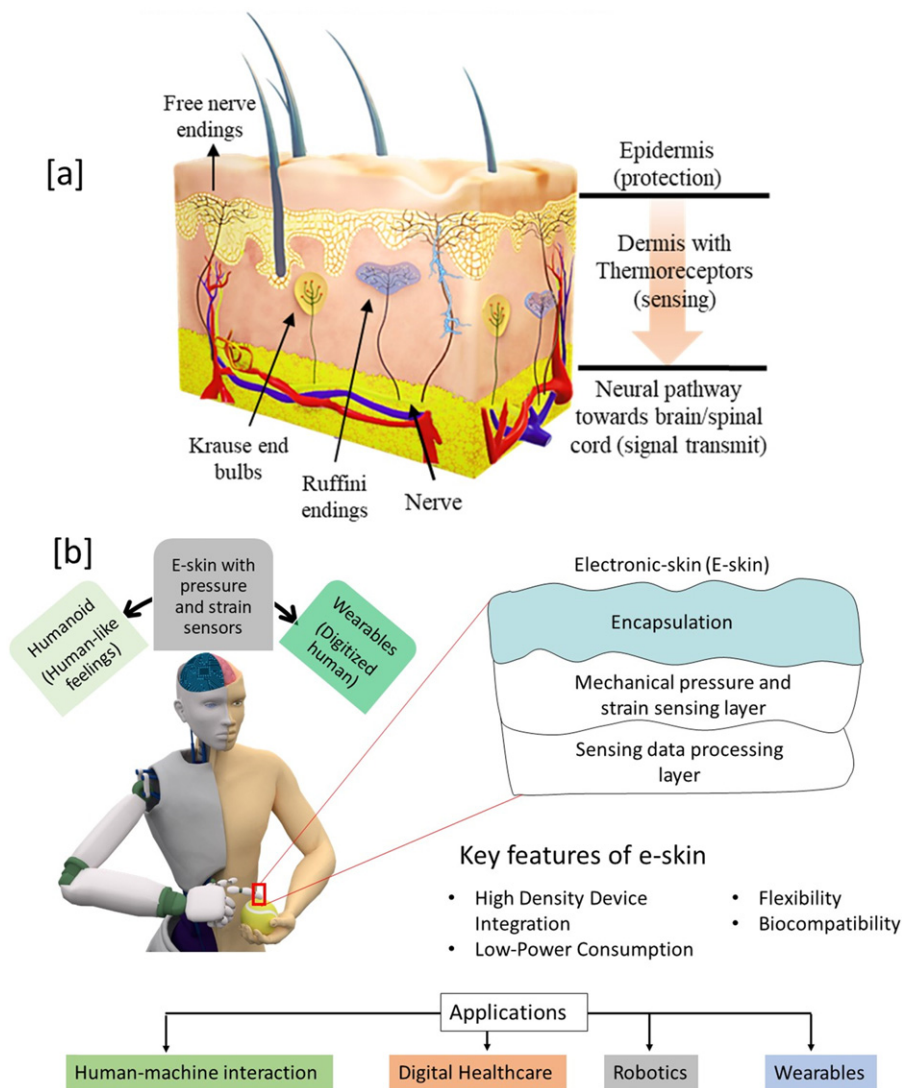


Fig. 1 (a) Schematic representation of skin model with various sensory receptors inside the soft tissue, (b) E-skin with mechanically soft pressure and strain sensors for wearables and to endow robots with human-like feelings. The figure also illustrates the key features needed for e-skin sensors such as high density of sensors, low power consumption, biocompatibility, flexibility etc. for applications in human-machine interactions, digital healthcare, smart wearables, and robotics. Reprinted from Neto, J., Chirila, R., Dahiya, A.S., *et al.*, 2022. Skin-inspired thermoreceptors-based electronic skin for biomimicking thermal pain reflexes. *Advanced Science* 9, 2201525.

robotics, prosthetics, human-machine interactive systems etc. It is also believed that e-skin will also have an impact on further advancement of the Internet-of-Things (IoT), connected vehicles (Murali *et al.*, 2022) and/or Internet-of-Medical-Things (IoMT) (Dahiya *et al.*, 2020c) where billions of devices will be connected for application areas such as smart cities and homes, intelligent in-vehicle interaction and digital healthcare. In many of these applications the soft pressure and strain sensors, mimicking skin morphology and functionalities of skin, are critical (Dahiya *et al.*, 2021).

In skin, various sensory receptors such as mechanoreceptors, thermoreceptors, etc. exist (Fig. 1(a)) to sense stimuli including pressure, temperature, and various others (Dahiya *et al.*, 2010, 2013; Navaraj and Dahiya, 2019; Dahiya and Valle, 2013; Neto *et al.*, 2022; Kumaresan *et al.*, 2021). Inspired from the skin, artificial, distributed mechanoreceptors and thermoreceptors have been fabricated to provide the sensory feedback (Neto *et al.*, 2022; Liu *et al.*, 2022b; Liu *et al.*, 2022a). Among them, the pressure sensors mimicking biological mechanoreceptors for haptic sensing or sense of touch or pressure have gained considerable prominence as they help provide artificial system for the human-like feelings (Fig. 1(b)) (Liu *et al.*, 2022b,a; Ntagios *et al.*, 2020b). The desirable key features of these sensors for e-skin are miniaturization (high device integration), light weight, low power consumption, flexibility, and biocompatibility, as summarized in Fig. 1(b). The recent advances in unconventional fabrication techniques such as microfluidics have opened interesting opportunities for cost-effective fabrication of soft and stretchable mechanical sensors and their incorporation in the e-Skin (Dahiya *et al.*, 2020a; Bhattacharjee *et al.*, 2020; Han *et al.*, 2018). The developed mechanical sensors such as strain and pressure can be mounted on skin and/or over robotic body or even integrated into clothing. The embedded sensing through the adoption of multi-material 3D printing offer potential to

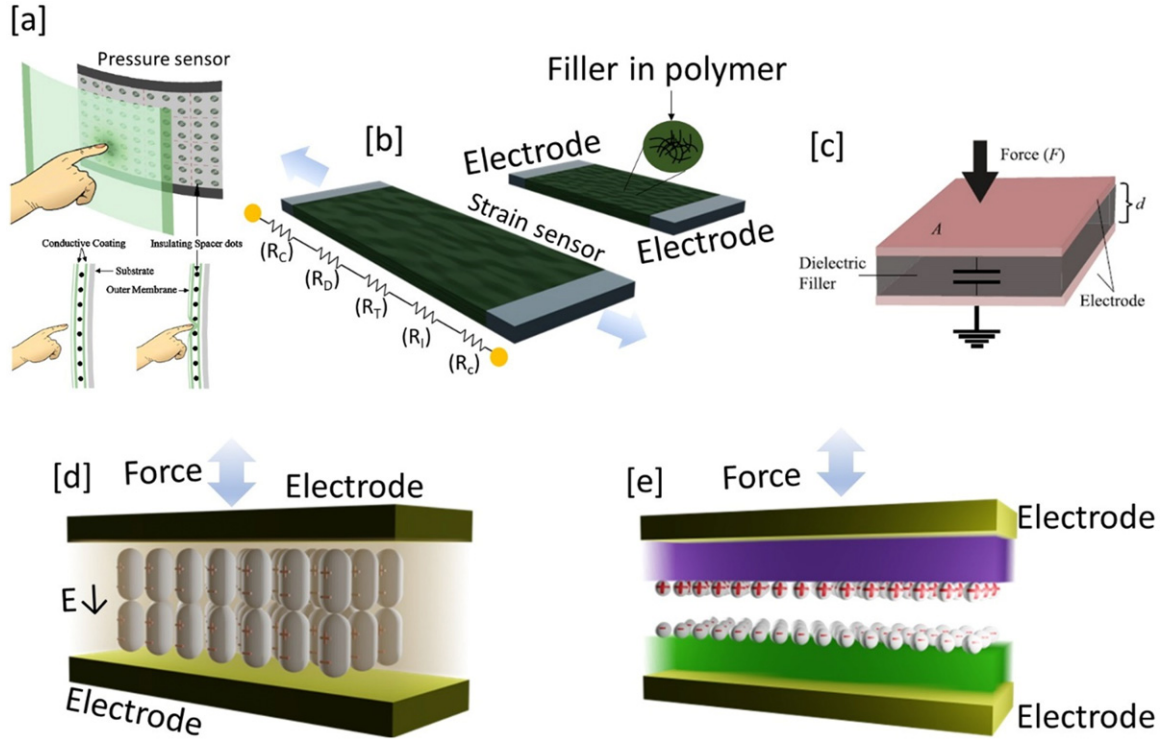


Fig. 2 Schematics illustrating the sensing mechanisms of (a) Resistive pressure, reprinted from (Dahiya and Valle), (b) resistive strain, (c) Capacitive, reprinted from (Dahiya and Valle), (d) Piezoelectric, and (e) Triboelectric. R_C is contact resistance, R_D is device dimensional resistance, R_T is tunneling resistance between two filler materials, and R_I is intrinsic resistance of the filler material. Reprinted from Dahiya, R.S., Valle, M. 2013. Robotic Tactile Sensing: Technologies and System. Springer Science + Business Media, Dordrecht.

develop robust and stable soft sensing structures for strain, stress, and contact estimation and also to realize printed interconnects (Ntagios *et al.*, 2020b; Chirila *et al.*, 2022; Chirila *et al.*, 2020; Nassar and Dahiya, 2021). Multi-material 3D printing offers advantages over conventional micron/nanofabrication technology in terms of resource-efficiency, digital (mask-less) fabrication, low-cost and potential of architecting electronic and multifunctional materials in a single run.

Exploring both manufacturing approaches i.e., microfluidics and multi-material 3D printing, mechanical sensors exploiting various sensing mechanisms including resistive, piezoresistive, piezoelectric and capacitive have been reported. In this regard, recent works such as embedded soft capacitive sensor and electronics for pressure-sensing, and embedded networks of piezoelectric, conductive, and structural elements to develop proprioceptive microrobots are worth mentioning (Ntagios *et al.*, 2020b). Lately, emerging transduction methods such as triboelectricity have been explored to meet new challenges and opportunities such as energy autonomy to broaden the applications of soft sensors in e-skin technology. The present chapter reviews these recent developments in e-skin and flexible electronics.

Sensing Mechanisms

Mechanical sensors such as strain and pressure sensors are developed using different transduction mechanisms such as resistive, piezoresistive, capacitive, piezoelectric, and triboelectric. Sensors based on resistive or piezoresistive and capacitance are more matured technologies, however, it is more difficult to achieve a high spatial resolution and they need external power supply to operate (Xu *et al.*, 2021; Ozioko *et al.*, 2021b; Karipoth *et al.*, 2021; Ntagios *et al.*, 2020b; Dahiya *et al.*, 2020a; Bhattacharjee *et al.*, 2020). Piezoelectric is also a mature technology and shows potential for self-powered sensors (Dahiya *et al.*, 2018; Ma *et al.*, 2022; Yogeswaran *et al.*, 2020). Lastly, triboelectric sensors are emerging as a self-powered technology based on triboelectrification, also called contact electrification effect (Min *et al.*, 2021d; Min *et al.*, 2021c; Min *et al.*, 2021b; Xu *et al.*, 2020; Khandelwal and Dahiya, 2022). The basic working mechanisms for these sensors are described in this section and shown schematically in Fig. 2.

Resistive

The fundamental operating mechanism of resistive sensors is they transduce mechanical deformations (e.g., because of pressure or strain) into electrical signals (Fig. 2(a-b)). Under applied uniaxial strains, the electrical sensing responses are characterized by Dahiya *et al.* (2020a):

$$\Delta R/R_0 = (R - R_0)/R_0, \quad (1)$$

where r_0 and r correspond to the original base device resistance (i.e., the resistance in the absence of mechanical stimuli) and the real-time resistance under mechanical deformation, respectively. The sensitivity for a typical resistive strain is quantified using the figure of merit, called the gauge factor (GF), which is defined as $GF = (\Delta R/R_0) / (\Delta l/l_0)$, where Δl is the change in the length and l_0 is the initial device length. Simplest of the resistive strain sensors are metal strain gauges but their sensitivity is low, typical values are between 1 and 5 and are developed on flexible substrates. To transfer the technology over a stretchable substrate (to accommodate more strain), for example on polydimethylphenylsiloxane (PDMS), metallic thin film with geometric patterns (e.g., serpentine or kirigami etc.) can be used. When the device is stretched, the geometrical change induces a change in dimensions, thus a change in the electrical resistance. To improve the sensitivity of metal based stretchable strain sensors, microcracking of the thin metallic films has been proposed and shown to exhibit promising results (Kang *et al.*, 2014). However, in such cases the device stability is also a big issue that remains to be resolved. To address this issue, nanocomposites (NCs) have gained attention (Karipoth *et al.*, 2021; Dahiya *et al.*, 2020a). The NCs are a mixture of viscoelastic materials (polymer) and conductive fillers (which can be one-dimensional (1D) or 2D nanomaterials or 3D scaffolds) (Fig. 2(b)). The sensors based on NC materials provide accurate and reliable sensing and they are also light weight and flexible/stretchable.

Piezoresistive

Piezoresistive sensors work very much similar to resistive sensors and respond to changes in pressure, bending, or force (Chirila *et al.*, 2022; Paul *et al.*, 2022; Ozioko *et al.*, 2021a). However, the changes in resistance of these sensors are due to variation in the energy bandgap of the material they use, when a mechanical load is imposed. Mathematically, the relationship can be expressed as:

$$\Delta R = R_0 \alpha P \quad (2)$$

where ΔR is the change in resistance, R_0 is the nominal unstressed base resistance, and α is the piezoresistive coefficient (m^2/N). A typical example of a piezoresistive sensor is demonstrated recently using the crumpled graphene flakes network (c-GFN) based pressure sensing field effect transistor (PRESSFET) (Paul *et al.*, 2022). The transistor device was designed to operate as a wearable switching device for the hands-free control of the robotic platform. The bandgap of 800 meV in c-GFN morphology helped to achieve distinct ON and OFF switching states in the pressure sensing range of 500–2500 Pa and allowed the use of PRESSFETs as a control device.

Capacitive

Alternative to resistive and piezoresistive sensing technology, capacitive sensors offer advantages such as higher linearity, less hysteresis, fast response time and simple readout electronics. Capacitive sensors are preferred for touch sensing on e-Skins, and they are also the popular touch interfaces in smartphones. The capacitive sensors can detect an applied force by measuring the change in capacitance of the sensor. The two most used capacitive device structures are, parallel plate structures and interdigitated structures (Ntagios *et al.*, 2020b; Núñez *et al.*, 2017; Dahiya *et al.*, 2015; Eswaran, 2013; Dahiya *et al.*, 2021). For the first type, two metallic/conductive plates are placed in parallel to each other separated by a dielectric material (Fig. 2(c)). The dielectric material can be a soft material, usually formed from a polymer, if the sensor is expected to have flexible form factor. This arrangement allows forces normal to the plates to be measured via monitoring the sensor capacitance, given by:

$$C = \epsilon \frac{A}{d} \quad (3)$$

Where ϵ is the dielectric constant of the dielectric, A is the surface area of the parallel plates and d is the distance between the plates.

The second type of capacitive sensors have interdigital structure. In this case, the capacitive sensor is a multi-finger periodic structure. The capacitance occurs across a narrow pathway between the two fingers/electrodes. The distance between the electrodes is extremely small while trying to utilize as much space as possible to extend the length of the gap between them. The capacitance of the structure is given by:

$$C = \epsilon * l[(N - 3) * A_1 + A_2] \quad (4)$$

Where ϵ is the dielectric constant, l is the length of the interdigital capacitor finger, N is the number of the fingers (Dahiya *et al.*, 2021). The pressure sensing is measured as a change in the capacitance of the device which occurs due to a change in the dielectric constant around the touched area.

Piezoelectric

Piezoelectric devices can also convert a mechanical input into an electrical signal (Nadaud *et al.*, 2018; Dahiya *et al.*, 2018; Oshman *et al.*, 2016). It works by the principle of electromechanical coupling. The piezoelectric sensor is based on effect, shown in Fig. 2(d), where materials have an ability to generate electrical charges under external applied mechanical force, pressure, or strain. Under an applied mechanical force, a piezo potential difference, between the top and bottom electrodes, is generated. The essence of the potential developed is the relative displacement of the cations and anions centers in the piezoelectric material, resulting in a microscale dipole moment (Hosseini *et al.*, 2020; Dahiya *et al.*, 2018). Polarization from all the domains, inside the material, results in a macroscopic potential, called "piezopotential," along the straining direction. Conventional piezoelectric sensors have

the advantage of being energy autonomous but are made of ceramics such as lead zirconium titanate (PZT) which lacks flexibility and have toxic lead content and thus, are not suitable for wearable applications. In the literature, in general, there are two different strategies reported to endow flexibility to piezoelectric devices: (i) employing intrinsically soft materials, and (ii) innovative engineering of device structure. Recent advances in the field of material science, nanoscience, and chemistry provide a promising option to develop flexible materials, such as inorganic nanomaterials, organic/inorganic hybrid networks and so on (Nadaud *et al.*, 2018; Dahiya *et al.*, 2018; Oshman *et al.*, 2016; Opoku *et al.*, 2015; Graton *et al.*, 2013). Alternatively, to maintain the high electrical performance of conventional rigid materials such as ceramics, geometric design engineering has been explored to obtain stretchable piezoelectric devices (Sun *et al.*, 2019). For instance, certain geometries such as zigzag, serpentine, kirigami, and horseshoe-shaped structures allow brittle functional and electrode materials including gold to be stretched out. Among both of these approaches, using different soft piezoelectric materials, including Glycine – Chitosan (Hosseini *et al.*, 2020), ZnO NWs (Opoku *et al.*, 2015) and poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) (Persano *et al.*, 2013) etc. have been exclusively explored to develop soft piezoelectric generators and sensors. These soft piezoelectric devices have been used as strain sensors and has shown great potential for real-time recording of physiological conditions and body motions. Stretchable strain sensors based on piezoelectric transduction mechanism have also been reported using organic/inorganic hybrid materials (Dahiya *et al.*, 2018). The device sensitivity to measure bending angles was demonstrated by wearing it onto a human index finger and monitoring the open circuit voltage while bending the index finger. A gentle strain induced by bending of the finger generated a peak open-circuit voltage of more than 3 V.

Triboelectric

The triboelectric nanogenerators (TENG) are an emerging technology and are attractive because of their simple designs, wide range of materials, and high energy outputs (Min *et al.*, 2021d; Min *et al.*, 2021c; Min *et al.*, 2021b). Moreover, the TENG has an edge over all other pressure sensors because of its self-powered nature and low-cost of fabrication. The working principle of the TENG is schematically shown in Fig. 2(e) (working under contact-separation mode). Tribo-charges are generated in accordance with the principle of contact electrification. The principle states that charge generation requires atoms across the interface pair to be within the repulsive regime (Li *et al.*, 2016; Wang and Wang, 2019). Since the first TENG report in 2012 (Fan *et al.*, 2012), significant progress has been made to realize flexible/stretchable TENGs based mechanical sensors (Xiong and Lee, 2019; Li *et al.*, 2020; Yao *et al.*, 2020; Chen *et al.*, 2019; Yang *et al.*, 2020). Two main factors have been explored in the literature to enhance the TENG performance and thus, the sensitivity, (i) choosing materials from the two extremes of the triboelectric (TE) series (one electro-positive and another electronegative) and (ii) modification of surface morphologies to enhance the contact area and. Hence the triboelectric effect. Using these approaches, soft skin-like TENGs have been developed for biomechanical energy harvesting and tactile sensing. The high performance soft TENGs were developed by hybridizing elastomer and ionic hydrogel as the electrification layer and electrode, respectively (Pu *et al.*, 2017). The developed self-powered pressure sensor showed ultrahigh stretchability (uniaxial strain, 1160%) and transparency (average transmittance, 96.2% for visible light). The output of the stretchable TENG was found to be pressure-sensitive (sensitivity of $\sim 0.013 \text{ kPa}^{-1}$), enabling their use in applications such as artificial e-skin for touch/pressure perception.

Further, it has been shown recently that TENG output can be tuned with the real contact area (A_r) and hence they could be used over a wide range of pressure sensing (Min *et al.*, 2021d; Min *et al.*, 2021a). For example, the A_r increases to 82% has been shown by increasing the pressure up to about 1200 kPa, after which it saturates. This means TENGs could be used as pressure sensor for up to 1200 kPa, which is sufficient to meet the operating requirements for applications such as wearables, humanoid robots (to help them stand and walk) and for sensing the impact force for water waves (Min *et al.*, 2022; Ntagios and Dahiya, 2022). Assuming that the tribo-charges are only generated through the changes in A_r , and defining σ_T as the areal density of transferred tribo-charges, the transferred charge (Q_T) can be defined as:

$$Q_T = \sigma_T A_r \quad (5)$$

the V_{oc} of the CS-TENG can be calculated, in accordance with the parallel plate capacitor model as:

$$V_{oc} = \frac{Q_T x(t)}{A_n \epsilon_0} \quad (6)$$

where, σ_T is the tribo-charges density, $x(t)$ is the separation distance, and the permittivity of air and the nominal contact area of interface pair is ϵ_0 and A_n , respectively. According to Eq. 5, the total tribo-charge generated Q_T is proportional to the applied pressures, as σ_T is constant for the selected active layers. Further, from Eqs. 5 and 6, V_{oc} depends directly on A_r . Thus, the contact pressure dependent variation in the V_{oc} is the mechanism for the wide range self-powered pressure sensing using TENG technology.

Fabrication Routes

A variety of approaches have been reported in the literature for the fabrication of mechanical flexible sensors, including standard lithography-based approach (Liang *et al.*, 2017). However, conventional approaches have limitations in terms of scaling-up as well

Table 1 Applications of pressure and strain sensors fabricated using microfluidic and 3D printing approaches. N/A – not available

<i>Fabrication method</i>	<i>Sensing mechanism</i>	<i>Sensing Material</i>	<i>Pressure/ Strain</i>	<i>Sensitivity, Gauge factor (GF)</i>	<i>Flexible/ Stretchable</i>	<i>Application</i>	<i>References</i>
Microfluidics	Resistive	CNTs	Strain	GF: 3–60	Stretchable	Robotic end-effectors	(Dahiya <i>et al.</i> , 2020a)
Microfluidics	Resistive	Ag NWs	Strain	GF: 1–10 ⁶	Stretchable		
Microfluidics	Resistive	PEDOT:PSS	Strain	GF: 12 000	Stretchable	Robotic end-effectors and wearable	(Bhattacharjee <i>et al.</i> , 2020)
Microfluidics	Resistive	Ag@CNTs	Strain	GF: 172	Stretchable	wearable (pronouncing detection)	(Pei <i>et al.</i> , 2019)
Microfluidics	Resistive	Ag NWs	Strain	GF: 2000	Stretchable	Wearable (monitoring facial expressions, pulse, body motion, and gestures)	(Han <i>et al.</i> , 2018)
Microfluidics	Resistive	Cu NWs	Strain	GF: 1678	Stretchable		
Microfluidics	Resistive	CNTs	Strain	GF: 800	Stretchable		
Microfluidics	Resistive	eGaN	Pressure	0.01 kPa ⁻¹	Stretchable	Hyperelastic pressure transducer	(Park <i>et al.</i> , 2010)
3D printing	Resistive	Silver palladium paste	Strain	GF: 1	Flexible	Knee joint motion analysis	(Nassar <i>et al.</i> , 2018)
3D printing	Capacitive	Silver paste	Pressure	0.25 kPa ⁻¹	Flexible	Fingertip for prosthetic hand	(Ntagios <i>et al.</i> , 2018)
3D printing	Capacitive	Ecoflex dielectric, graphite ink electrodes	Pressure	0.00348 kPa ⁻¹	Flexible	Fingertip for prosthetic hand	(Ntagios <i>et al.</i> , 2020b)
3D printing	Resistive	Graphite paste	Pressure	0.346 kPa ⁻¹	Flexible	Fingertip for prosthetic hand and electromagnetic microactuation	(Ozioko <i>et al.</i> , 2021a)
3D printing	Capacitive	PI-ETPU electrodes and EcoFlex as dielectric	Pressure	2.4 MPa ⁻¹	Flexible	Shoe insole for gait analysis	(Ntagios and Dahiya, 2022)
3D printing	Resistive	Conductive silicone rubber filled with silver-coated glass fiber	Strain	N/A	Flexible	Soft robotics and wearable electronics	(Huang <i>et al.</i> , 2018)
3D printing	Resistive	PU/MWCNT	Strain	GF: 8.6–176	Stretchable	N/A	(Christ <i>et al.</i> , 2017)
3D printing	Resistive	AgNP/HCNT/PU	Strain	GF: 2.9–4.3 × 10 ⁴	Stretchable	Wearables (diverse joint movements and facial motion)	(Xiang <i>et al.</i> , 2020)
3D printing	Resistive	Copper/nichrome/PLA	Strain	GF: 1.13–1.17	Stretchable	structural health monitoring	(Saleh <i>et al.</i> , 2019)

as huge chemical and electronic waste. As a result, the unconventional fabrication routes are also gaining interest (Dahiya *et al.*, 2022b,a; Shakhthivel *et al.*, 2021; Dahiya *et al.*, 2020b). For instance, simply injecting active sensing material into microfluidic channels in a wide range of soft substrates (Dahiya *et al.*, 2020a; Bhattacharjee *et al.*, 2020) allows for inexpensive and fast fabrication of devices outside of a cleanroom and without the need for vacuum processing. Similarly, low cost and resource-efficient 3D printing fabrication approaches have been experimented to develop robust mechanical soft sensors and interconnects (Ntagios and Dahiya, 2022; Nassar and Dahiya, 2021; Ntagios *et al.*, 2020b). In this chapter, we have focussed on mechanical sensors fabricated using microfluidics and 3D printing and their application in e-skin, as summarized in **Table 1**.

Microfluidics

Microfluidic techniques have been used mainly to design and fabricate strain sensors having a high sensitivity and with enhanced stretchability. Ideally, a wearable sensing device should have a large stretchability as well as a high GF. The fabrication method is inspired from a micromolding in capillary (MIMIC) process (Kim *et al.*, 1996), schematically shown in the **Fig. 3**. In the first step, the grooved bottom stretchable plate of elastomeric materials such as Ecoflex, PDMS, Dragon skin etc. is realized using a standard molding process. The groove dimensions and depth can be tuned according to the size and thickness of resist layer and/or other materials such as polyimide. For example, a feature size of 100 µm was obtained using a standard photolithography process employing SU-8 negative resist whereas macro size features were developed using standard Kapton tape (Dahiya *et al.*, 2020a). In the step ii, suspension of nanomaterial as filler or other novel conductive liquid is injected into the micro/macro fluidic channels. The suspension filled the channels of the mold through capillary forces wherein the rate of capillary filling depends on the kinematic viscosity, surface tension of the liquid, and section size of the capillary. To improve the wettability of filler materials, to the elastomeric polymers, oxygen plasma treatment could be carried out before injecting the suspension. The filler material is usually consisting of 1D materials, such as CNTs or metallic silver (Ag) or copper (Cu) NWs, which offers potential to realize stretchable strain sensors with high GF. In the third step, Cu wires are attached. In the last step, a “sandwich” structure is realized by pouring another layer of elastomeric polymers which flows into the connected filler network and

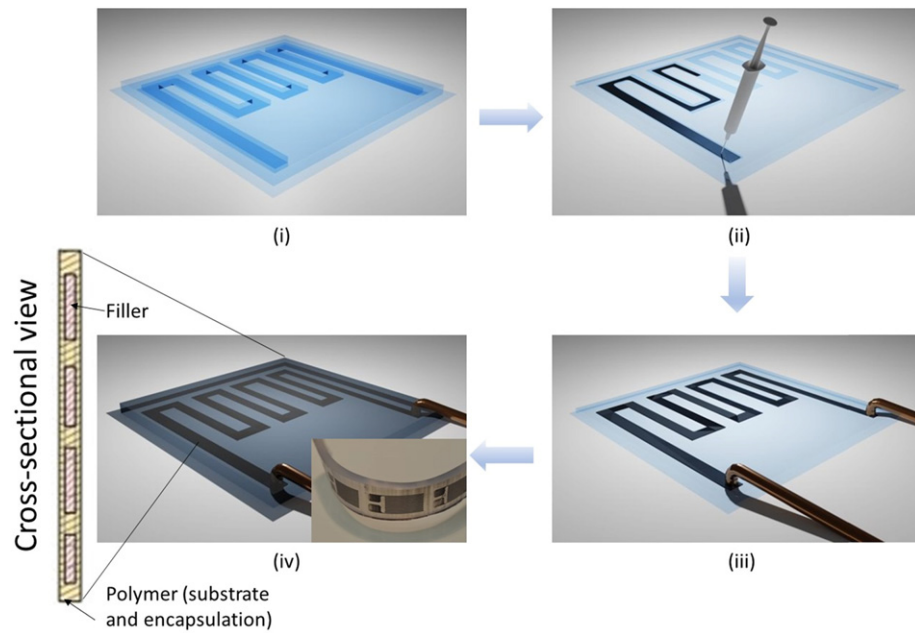


Fig. 3 Schematic of the microfluidic based fabrication process of the stretchable mechanical sensors. Step (i) Fabrication of capillaries, (ii) filling the capillaries with filler suspension, (iii) connecting Cu interconnects, and (iv) encapsulation. The inset in step iv also shows an optical micrograph of a typically fabricated device using microfluidic based approach and a cross-sectional view of the final device.

crosslinked with the bottom layer. The top elastomeric layer will fully and firmly encapsulate the sensing material, and thus improve the robustness of the device.

There are two important and interesting features that have been identified for the microfluidic based fabrication process by [Dahiya et al. \(2020a\)](#). First, 1D nanomaterials are uniformly percolated within polymer, a feature that was difficult to obtain in conventional NC materials. For instance, generally, to disperse CNTs in a polymeric medium, a disentanglement procedure is needed. So far, most of the research is focused on the development of disentanglement/alignment methods of 1D structures such as CNTs in a polymeric medium. The process requires a long time to get dry CNTs to be wetted especially when CNTs are in contact with an incompatible fluid. Second, NCs can achieve an insulator/conductor transition when the filler content is high enough to build up the percolated conductive networks throughout the polymer matrix. In a microfluidic based approach, the amount of filler material is negligible compared to the organic part, making it a resource efficient and low-cost fabrication process.

Multi-Material 3D Printing

3D printing is a well-known technology for creating bespoke designs and rapid prototyping. Additive manufacturing, specifically 3D printing (also known as multilayer printing), provides a significant amount of freedom to designers compared to other approaches including conventional ones and as a result, complex designs can be developed with 3D printing at low cost. Fingertip patterns have been developed using 3D printing, and used alongside neural networks to dynamically classify different surfaces ([Navaraj and Dahiya, 2019](#)). 3D printing has provided researchers with new and efficient tools to enhance the capabilities of e-skins and tactile sensors. Particularly, the multi-material 3D printing approach used to realize flexible sensors offers advances over current additive manufacturing strategies ([Ntagios et al., 2020b](#); [Ozioko et al., 2021b](#)). This is because a combination of multiple materials can be extruded to realize a tactile feedback mechanism with embedded electronics and sensors in 3D space in one go.

As an example of multi-material fused deposition modeling (FDM 3D-printing), the process outlined in ([Ntagios et al., 2020b](#)) provides an accurate baseline for the design and fabrication principles of embedding sensing elements in printed components (**Fig. 4**). The illustrated approach was used to fabricate a 3D printed hand with embedded soft capacitive touch sensors for interacting with everyday objects. Firstly, a structural base is fabricated using structural materials, typically thermoplastic polymers such as polylactic acid (PLA) or Acrylonitrile butadiene styrene (ABS). Second, electronic components are embedded into the structure to provide electronic functionality to the produced device. The next step typically requires printing electrically conductive functionalized materials to connect the previously embedded electronic components. Lastly, the device is encapsulated using non-functional materials to provide robustness to the device and protect it from potential external stresses. This approach allows for design flexibility and freedom regarding the nature of the sensor being fabricated and its mechanical specifications. Specific materials can be chosen to optimize various design parameters such as mechanical strength, flexibility, and weight, without a significant impact on fabrication costs or times.

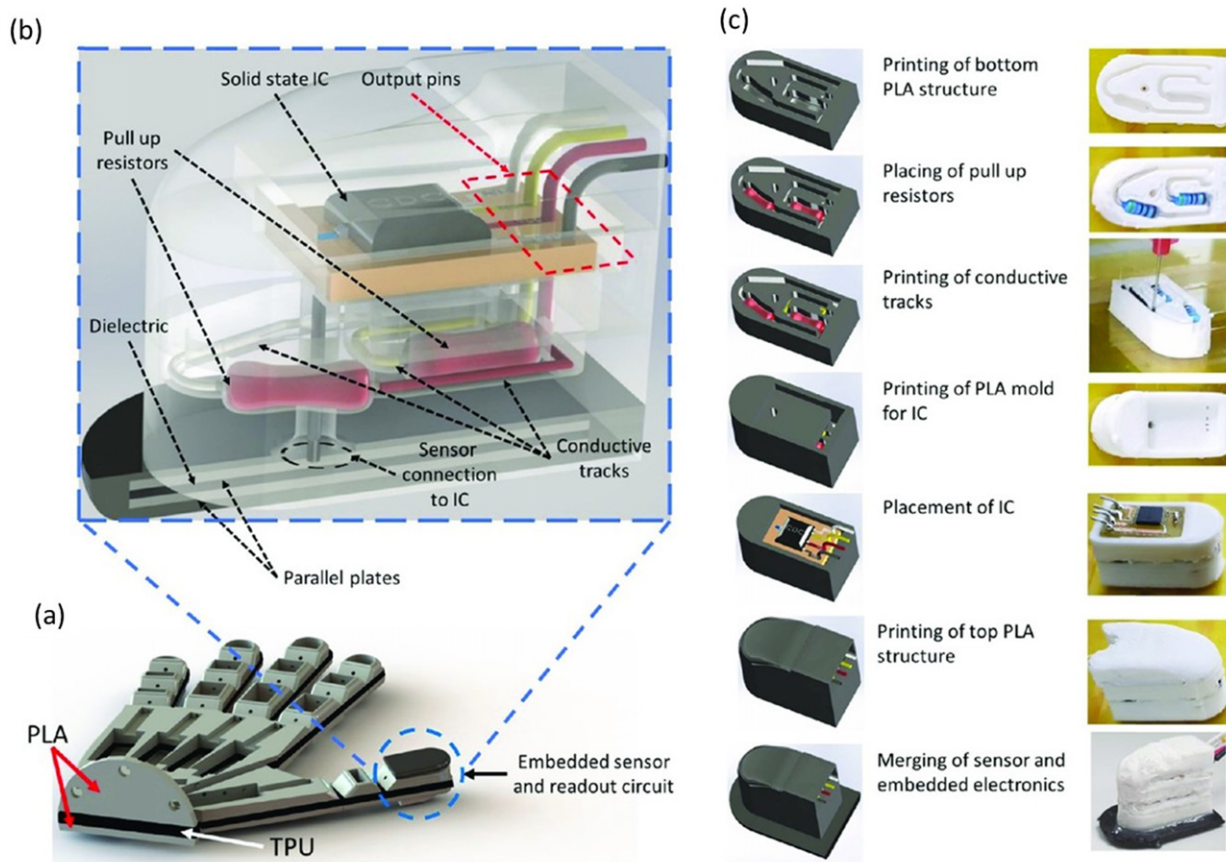


Fig. 4 Multi-material 3D printing technique to fabricate embedded mechanical sensors. The 3D printed hand with intrinsic tactile sensing. (a) CAD design of the hand with the smart sensing phalanx having a soft capacitive touch sensor and an embedded readout circuit. (b) CAD design of the interior structure of the phalanx. (c) Fabrication steps for the 3D printed phalanx. The Figure is reprinted from Ntagios, M., Nassar, H., Pullanchiyodan, A., Navaraj, W.T., Dahiya, R., 2020b. Robotic hands with intrinsic tactile sensing via 3D printed soft pressure sensors. *Advanced Intelligent Systems* 2, 1900080.

Application of Soft Mechanical Sensors-Based E-Skin

An e-skin consisting of multiple soft mechanical sensors (pressure, strain, tilt, etc.) has shown to bestow robots and prostheses with a sense of human-like touch. This is important in robots which are designed to carry out delicate tasks, e.g., automated sorting of soft objects. Both 3D printing and microfluidic based fabrication approaches have recently attracted wide attention to fabricate soft mechanical sensors-based e-skin. Microfluidics have been mainly used to develop soft stretchable strain sensors and offer huge potential because of their ability to monitor and sense vital physiological signals (Fig. 5). Further, because it is a cost-effective and resource-efficient approach, and resulting into highly compliant wearable sensors, the microfluidic-based fabrication is gaining significant attention. For example, 1D CNTs and Ag NWs were used as filler materials to fabricate NC-based stretchable strain sensor (Fig. 5(a-e)) (Dahiya et al., 2020a). The fabricated strain sensors using CNT/dragon-skin NC exhibits a wide sensing range (2%–180%), and moderately high sensing performance with outstanding durability (over 6000 cycles). The wide sensing range was attributed to the connected networks of CNTs which could accommodate high mechanical strain under stretching. These sensors were applied for human motion monitoring such as finger, knee, and wrist bending movements to enable human physiological parameters to be registered and analysed continuously (Fig. 5(f)). They are also employed in multichannel and interactive electronic systems as a control mechanism for teleoperation for robotic end-effectors (Fig. 5(g)). The Ag NW-dragon-skin NC based strain sensors showed very high sensitivity ($GF = 10^7$). However, sensing function for Ag NW-dragon-skin NC-based sensors is limited within a very narrow range (0%–30% strain) because of their brittle nature. Therefore, these strain sensors (Ag NW-dragon-skin NC) cannot monitor external stimuli with large strain. Extending further, the microfluidic fabrication technique was used to inject poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) polymer in a PDMS channel with a diameter $\approx 175 \mu\text{m}$ (Bhattacharjee et al., 2020) (Fig. 5(h-i)). The presented approach is interesting as it avoids the use of filler materials such as Ag NWs or CNTs completely which requires sonication steps for disentanglement. The sensor exhibits a three order ($\Delta R/R_0 \approx 1200$) increase in the resistance for 10% applied strain. This leads to a GF of $\approx 12,000$, which is about 400 times higher than most of the reported polymer-based flexible strain sensors. Using this sensor, application in robotics and

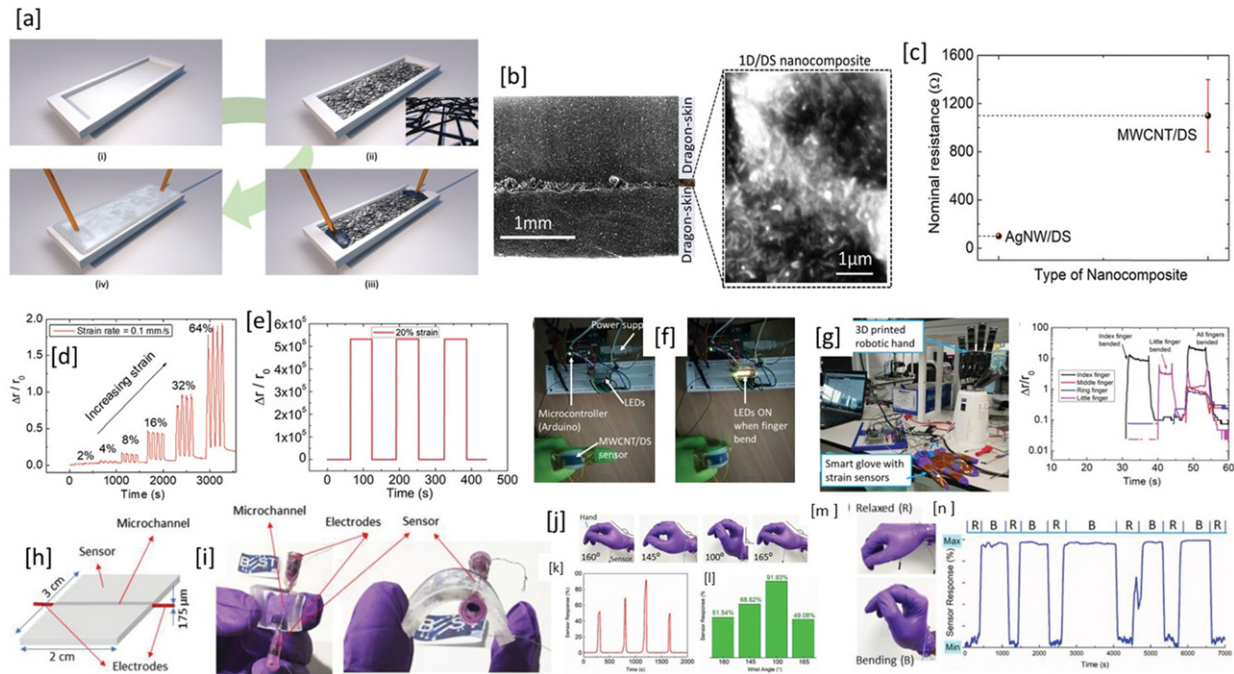


Fig. 5 Stretchable strain sensors fabricated using microfluidic technique based on the resistive and piezoresistive transduction method: (a-g) CNT and Ag NWs based nanocomposites for human movement monitoring and robotic applications (a) Schematic of the fabrication process, (b) Cross-sectional SEM images of the sensor illustrating network of CNTs encapsulated in Dragon Skin (DS) polymer, (c) Average nominal device resistance of the multi-walled carbon nanotubes (MWCNTs)/DS and silver nanowires (AgNWs)/DS nanocomposite materials, (d) relative change in resistance when strained from 2% to 64% for CNT/DS NC, (e) Relative change in resistance for Ag NW/DS NC when strained to 20%, (f) illustration of finger movement monitoring with an integrated electronic system constructed using a microcontroller, LEDs and strain sensor placed on the index finger. Optical image showing LEDs “off” when no strain is applied to the sensor (zero degree bending of the finger) and LEDs turn “on” when strain is applied to sensor on 90° bending of the finger, and (g) optical image of the test-bench set-up for the MWCNT/DS strain sensors to be used as a control mechanism for teleoperation for robotic end-effectors and a graph depicting the relative change in the resistance of the sensor while bending fingers. (h-n) poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) polymer in microchannels to remotely control the robotic hand movements: (h) the schematic illustration of the fabricated strain sensor; (i) the optical image of the flexible sensor, (j) optical image of the hand bent at different angles; (k) the temporal response of the sensor due to the bending; (l) response of the sensor for different bending angles; (m) experimental condition of relaxed (R) and bending (B) condition, and (n) temporal response of the sensor for different holding times at maximum bending (B) condition. Reproduced from Dahiya, A.S., Gil, T., Thireau, J., *et al.*, 2020a. 1D nanomaterial-based highly stretchable strain sensors for human movement monitoring and human-robotic interactive systems. *Advanced Electronic Materials* 6, 2000547. Bhattacharjee, M., Soni, M., Escobedo, P., Dahiya, R., 2020. PEDOT:PSS microchannel-based highly sensitive stretchable strain sensor. *Advanced Electronic Materials* 6, 2000445.

wearable systems were demonstrated (Fig. 5(j-n)). The authors have used sensor feedback from human hand to remotely control the robotic hand movements. The microfluidic fabrication approach could also be used to flow liquid metals and other novel conductive liquids in microchannels to obtain higher stretchability and robustness (Soomro *et al.*, 2022).

Along with the microfluidic approach, 3D printing technology has been exclusively used to fabricate soft pressure and strain e-skin sensors. The 3D printed soft sensors are revolutionising a wide range of applications including medical, soft robotics, human-machine interactions (HMI) and the Internet of Things (IoT). For instance, 3D printing was used to construct sensors for gait monitoring (Ntagios and Dahiya, 2022), knee joint motion analysis (Nassar *et al.*, 2018) and as wearables for rehabilitation (Ozioko and Dahiya, 2022; Beckerle *et al.*, 2017; Ozioko *et al.*, 2017), and for smart prosthetic limbs (Devaraj *et al.*, 2018; Kawasaki *et al.*, 2002; Ntagios *et al.*, 2020b). Among various 3D printed sensors, pressure and strain sensors have shown substantial potential (Table 1). Due to the nature of robotic applications today, monitoring pressure could provide critical information regarding the external environment and how the robotic system is performing. While monitoring pressure from a larger surface, e.g., in the context of an array of an e-skin, critical information can be inferred from the ambient environment. Recent research has shown that super-resolution can be achieved through an e-skin consisting of a finite number of pressure sensors (Yan *et al.*, 2021). Using this sensor arrangement, force can be separately measured, thus providing a robot with more information about its environment.

3D printing has also shown huge potential to bring novel features in prosthetics. Because of the recent advances in multi-material 3D printing, robotic hands were fabricated which not only could sense pressure, but also compute the optimal way of grasping objects (Romano *et al.*, 2011; Allen *et al.*, 1993; Tawk *et al.*, 2022; Laffranchi *et al.*, 2020), slip detection (Navaraj *et al.*, 2019; Iskrouos and Thakor, 2019; Tomar and Tadesse, 2016) or even used to understand and map the texture of an object

(Luo *et al.*, 2017; Johannes *et al.*, 2020). 3D printed pressure sensors have also greatly increased the performance of multimodal sensing systems for prosthetic hands (Polishchuk *et al.*, 2016; Allen *et al.*, 1997) and e-skins (Kumaresan *et al.*, 2021). Integrating multiple sensor devices would not be an ideal choice for wearables also due to the complexities of assembly and calibration and moreover, lack of comfort for the users as it will add weight. For rehabilitation, pressure sensors have been instrumental in manufacturing bespoke solutions for individual patients. Since the design and fabrication of sensory systems is not hindered by manufacturing related limitations such as change of design constraints, cost etc., unique, and complex designs can be explored. In the case of gait analysis, a sensor array in the shape of a shoe insole was used (Ntagios and Dahiya, 2022). In this case, indeed, the design of the sensor will vary from patient to patient, but the sensing mechanism is similar. Additionally, for prosthetic limbs, the size and shape of the device will vary, yet the sensorisation could be achieved without completely redesigning the device prototype, thus a customized design could be 3D printed easily. Ultimately, this practice drastically reduces the design time required as well as the costs associated with manufacturing.

Challenges and Future Outlook

Energy Autonomy

The self-powering of sensors and electronics on e-skin is desirable for applications such as wearables, robotics, and digital healthcare. However, it has been a significant challenge for engineers and scientists to find efficient strategies to supply power for continuous operation of wearable sensors. This is because the current matured energy harvesting technologies are in a rigid form factor. Currently, supplying electrical power to wearable sensors is done by using conventional rigid lithium batteries which have limitations such as large size and weight, frequent replacements, toxicity etc. Alternative approaches for energy harvesting are being investigated where electrical energy is harnessed from the ambient (solar cells, thermoelectric, piezoelectric, triboelectric or combination of sources through hybrid generators) or kinetics (body dynamic movements) using flexible energy harvesters that can be stored in tandem with a rechargeable and stretchable batteries and supercapacitors (Dahiya *et al.*, 2020c; Escobedo *et al.*, 2021; Manjakkal *et al.*, 2019). However, design and integration of all these devices on a common flexible/stretchable platform comes with new challenges.

Integrating self-powered sensors could also be a way forward which can significantly reduce the energy dependence on batteries/supercapacitors. Tactile/strain/pressure sensing in e-skin is endowed mainly by resistive, piezoresistive and/or capacitive sensors which requires external power to carry out sensing functions. On the other hand, as described in this chapter, PiezoElectric NanoGenerators (PENGs) and TriboElectric NanoGenerators (TENGs) are emerging technologies which can generate electrical signals from mechanical bending. The magnitude of the electrical signals can thus be correlated to the intensity of the external mechanical stimuli, which endows PENG and TENG sensors with the feature of being self-powered. Exploiting resource-efficient 3D printing fabrication approaches, stretchable kirigami PENGs have shown promising results. The 3D printable piezoelectric ink is formulated of materials including barium titanate (BaTiO₃) nanoparticles, and Poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) matrix, and silver flakes-based electrodes are also 3D printed (Zhou *et al.*, 2020). Further, a multimodal ferrofluid-based TENG, featuring sensing capabilities to a variety of hazard stimuli such as a strong magnetic fields, noise levels, and falling or drowning has also been reported (Ahmed *et al.*, 2019). The developed TENG consists of a deformable elastomer tube filled with ferrofluid, as a triboelectric layer, surrounded by a patterned copper wire, as an electrode, endowing the TENG with excellent waterproof ability, conformability, and stretchability (up to 300%). It could be interesting if microfluidic approaches could be explored in this case to realize such a ferrofluid-based TENG to achieve smart multifaceted energy autonomous sensing structures for diverse applications including hazard preventive wearables, and remote healthcare monitoring.

Robustness

Past generations of mechanical sensors lack robustness and exhibit inconsistent readout behaviors due to mechanical fatigue or wear and tear (Chortos *et al.*, 2016; Wang *et al.*, 2015; Dahiya *et al.*, 2010). This is because first generations of e-skin sensing technologies, particularly for robotic applications, comprised simply of a flexible sensing system wrapped around a rigid robotic body. Due to a drastic reduction in sensor displacement driven by the rigid body the e-skin was attached to, such sensing systems were unsuitable to use in hazardous environments. Further, the wires/interconnects were exposed to ambient condition and lead to extremely noisy output signals. In many cases, the sensing elements of such a rudimentary design were in contact with sharp objects and could often get damaged and stop working correctly (Polishchuk *et al.*, 2016; Wang *et al.*, 2018; Kawasaki *et al.*, 1999; Kawasaki *et al.*, 2002). These issues arise from wrapping the e-skin directly to the rigid surfaces of robots and amplified in areas with the highest displacement.

To alleviate some of these problems, later research has focused on implementing soft enclosures for the e-skins i.e., embedding the device components within a soft polymeric layer. These designs range from simple polymers which provide an additional layer of protection for the sensors (Shimojo *et al.*, 2004; Wettels *et al.*, 2008) to more complex solutions. In some cases, sensory e-skins are integrated into rigid bodies, and in some cases they even integrate electronic components and other sub-systems (Fishel and Loeb, 2012). Enclosures have also eliminated some of the other issues related to e-skins, such as temperature dependence and exposure to UV radiation. This approach, combined with recent advancements in 3D printing and material science and have

resulted in new generation of mechanical sensors made via multi-material 3D printing (Truby *et al.*, 2019; Ntagios *et al.*, 2020a; Gao *et al.*, 2019). These advancements have resulted in 3D printed intelligent fingertips for robots that not only are able to sense but also digitalize the information for maximizing the use of space and drastically reducing the fabrication costs. Employing 3D printing to construct the embedded sensors and electronics, the issues regarding device integration, including routing of wires in smart gloves, robotic hands etc. could be addressed.

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Piezoelectric Actuators

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Abstract

Piezoelectric actuators have been commercialized in various smart structures and systems such as precision positioners, adaptive mechanical dampers and piezoelectric energy harvesting, and miniature ultrasonic motors. This article describes fundamentals of piezoelectricity, and developments of piezoelectric actuators in terms of actuator materials, device designs, drive/control techniques, modeling and applications.

Key Points

- Learn the fundamentals of piezoelectricity (constitutive equations, electromechanical coupling factor, electrostriction, resonance/antiresonance dynamic analysis).
- Piezoelectric loss factors and mechanical quality factors.
- Energy transmission coefficient.
- Piezoelectric actuator materials (high-power piezoelectrics, PZT, Pb-free piezoelectrics, photostrictive materials, phase change materials).
- Piezoelectric device designs (multilayer, bimorph, cymbal).
- Ultrasonic motors, impulse motors.

Introduction

This article reviews piezoelectric actuators, started from the fundamentals of piezoelectricity. Then, actuator materials introduce PZT and related high-power piezoelectrics, phase-change ceramics, photostrictive ceramics, and piezoelectric composites (damping and magnetoelectric materials). Actuator device designs illustrate multilayer, bimorph, cymbals and thin-film MEMS. Actuators are driven/controlled by unique techniques such as negative capacitance components, asymmetric rectangular voltage, and pulse width modulation. We will also review representative applications: deformable mirrors (positioner), inkjet printers (impact motor), diesel injection valves (impact motor), micro metal-tube motors for camera modules (ultrasonic motor).

Why Piezoelectric Actuators?

Piezoelectric ceramics have formed a new field between electronic and structural ceramics (Uchino and Nomura, 1983a; Uchino, 1993, 1994, 2009, 2020). Application fields are classified into three categories: positioners, motors and vibration suppressors. The manufacturing precision of optical instruments such as lasers and cameras, and the positioning accuracy for fabricating semiconductor chips, which must be adjusted by actuators, is of the order of 0.1 μm , which the conventional gear machines cannot reach. The conventional electromagnetic motors are still dominant in large machine market, but their efficiency drops significantly with reducing the motor size due to the Joule heat by thin copper-wire coil, such as 30% for 30 W motors. Piezoelectric ultrasonic motors whose efficiency is insensitive to size (typically 30%) are superior in the mini-motor area (that is, portable equipment operated by batteries). Vibration suppression in space structures and military vehicles using piezoelectric actuators, as well as energy harvesting, is also another promising technology using piezoelectric actuators.

The advantages of piezoelectric actuators over counterpart electromagnetic (EM) types are summarized:

- (1) More suitable to miniaturization –

From the market research result, tiny motors in the range of 5–8 mm are highly required for the office and factory automation equipment; while 1–3 mm are desired for the medical apparatuses. However, due to the Joule heat generation from the copper-wire coil, the conventional EM motors are rather difficult to produce with sufficient energy efficiency in these miniature motor areas. Fig. 1 shows motor characteristics for hundreds of commercial electromagnetic (EM) motors: specific power ($\propto$ efficiency) vs. power ($\propto$ actuator size) [Data in the year 1988, unpublished] (Uchino, 2020). The significant decrease in the efficiency of the EM motor is mainly due to the Joule heat increase in reducing the coil wire thickness. Since the stored energy density of the piezo-device is larger than that of an EM type, 1/10 smaller in volume and weight can be achieved for micro motors.

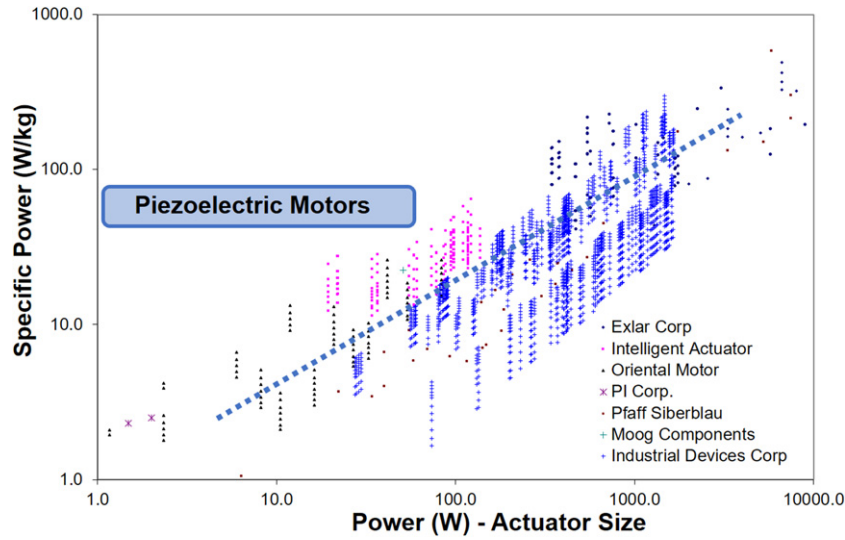


Fig. 1 Efficiency versus power relation for electromagnetic and piezoelectric motors.

- (2) No electromagnetic or sound noise generation –

Since no magnetic jam shielding is necessary, we can keep a compact design. This is the reason why the launching switch of nuclear-bomb missiles are made by piezoelectric ultrasonic motors. No EM noise generation is a benefit for the human interfaces such as smart phones, headsets not to increase the brain cancer risk. Also, because of no gear-box requirement, the ultrasonic motors (USMs) are operated very quietly for human ears, as long as they are driven by inaudible high frequency. This is the reason why the camera zoom/focus mechanisms introduced the USMs preferably.

- (3) Higher efficiency –

As shown in Fig. 1, though the EM motors are much superior in kW or higher power level, a significant decrease in the efficiency occurs in the motor size reduction. For example, more than 90% of the input electrical energy in a wrist-watch motor (~ 1 W) is spent to generate heat (dramatical efficiency reduction)! On the other hand, since the efficiency of the piezoelectric motors is insensitive to the size ($\sim 30\%$), the USMs are effective in the power range lower than 30 W; that is, for portable devices.

- (4) Non-flammable –

The reader is familiar with the burning accident of EM motors in refrigerators, vacuum cleaners etc. The piezoelectric motors and transformers are much safer in general for the overload or the short-circuit at the output terminal. Because the piezo-motor temperature rise under overloading changes the piezoelectric resonance frequency, which automatically stops the motor operation, leading to cooling down and the motor recovery after some minutes later. We sometimes call this “homeostatic”.

Fundamentals of Piezoelectricity

Let us review fundamental of piezoelectricity first. (1) crystal structures, (2) microscopic origins of electric field induced strains, and (3) piezoelectric constitutive equations, and electromechanical coupling factors are described in this section.

Crystal Structures

In the so-called dielectric (i.e., resistive) materials, the constituent atoms are considered to be ionized to a certain degree and are either positively or negatively charged. In such ionic (and some covalent) crystals, when an electric field is applied, cations are attracted to the cathode and anions to the anode due to electrostatic interaction. The electron clouds also deform, causing electric dipoles. This phenomenon is known as electric polarization of the dielectric, and the polarization is expressed quantitatively as the sum of the electric dipoles per unit volume [C/m^2]. Compared with air-filled capacitors, dielectric capacitors can store more electric charge due to the dielectric polarization P . The physical quantity corresponding to the stored electric charge per unit area is called the electric displacement D , and is related to the electric field E by the following expression:

$$D = \epsilon_0 E + P = \epsilon_0 \epsilon_r E \quad (1)$$

Here, ϵ_0 is the vacuum permittivity ($= 8.854 \times 10^{-12}$ F/m), ϵ_r is the material's relative permittivity (also simply called permittivity or dielectric constant, and in general is a tensor parameter). Because of the induced polarization P , a couple of orders of magnitude larger free charge can be stored in an electrode dielectric capacitor (Uchino, 2009).

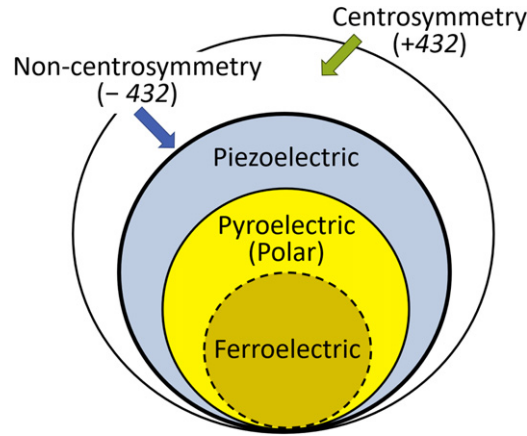


Fig. 2 Classification of dielectrics according to crystal centro-symmetry and polarity.

Depending on the crystal structure, the centers of the positive and negative charges may not coincide even without the application of an external electric field. Such crystals are said to possess a “spontaneous polarization” (or “pyroelectric”). When the spontaneous polarization direction of the dielectric can be reversed by an electric field, it is called “ferroelectric”. Not every dielectric is a ferroelectric. Crystals can be classified into 32 point-groups according to their crystallographic symmetry, and these point groups can be divided into two classes, one with a center of symmetry and the other without. There are 21 point-groups which do not have a center of symmetry, as shown in **Fig. 2**. In crystals belonging to 20 of these point groups [point group (432) being the sole exception], positive and negative charges are generated on the crystal surfaces when stresses are applied (i.e., “direct piezoelectric effect”), which are known as “piezoelectrics”. 10 point-groups among piezoelectrics possess spontaneous polarization (i.e., polar, or pyroelectric). “Pyroelectricity” is the phenomenon whereby, as the temperature of the crystal is changed, electric charges corresponding to the change of the spontaneous polarization appear on the surface of the crystal. Among the pyroelectric crystals, those whose spontaneous polarization direction can be reversed by an electric field (not exceeding the breakdown limit of the crystal) are called “ferroelectrics”. Thus, there is some experimental ambiguity in this definition; in establishing “ferroelectricity”, it is necessary to apply an electric field to a pyroelectric material and experimentally ascertain the polarization reversal.

Microscopic Origin of Field Induced Strains

Solids, especially ceramics (inorganic materials), are relatively hard mechanically, but still expand or contract depending on the change of the input parameters. The “strain” (defined as the “displacement” ΔL /initial length L) caused by temperature change or stress is known as “thermal expansion” or “elastic deformation”, respectively. In insulating materials, an electric field application can also cause deformation, which is called “electric field induced strain”. There are three kinds: “piezoelectric strain”, “electrostriction”, and “domain-reorientation-based strain”. We consider the microscopic origin below. The “converse piezoelectric effect” is defined as a primary electromechanical coupling effect, that is, the strain is proportional to the electric field; while “electrostriction” is a secondary coupling in which the strain is proportional to the square of the electric field. Thus, they are distinguished. However, the piezoelectricity of a ferroelectric, having a centrosymmetric prototype phase at an elevated temperature, is considered to originate from the “electrostrictive coupling”, hence these two effects are related.

Piezoelectric strain

Why a strain is induced by an electric field is explained herewith (Uchino *et al.*, 1981; Uchino and Nomura, 1983b). For simplicity, let us consider a diatomic ionic crystal such as NaCl. **Figs. 3(a)** and **3(b)** show a 1D “rigid-ion spring model” of the crystal lattice. The springs represent equivalently the cohesive force resulting from the electrostatic Coulomb energy and the quantum mechanical repulsive energy. **Fig. 3(b)** shows the centrosymmetric case, whereas **Fig. 3(a)** shows the more general non-centrosymmetric case. In (b), the springs joining the ions are all the same, whereas in (a), the springs joining the ions are different for the longer and shorter ionic distances, in other words, hard and soft springs existing alternately are important. Next, consider the state of the crystal lattice (a) under an applied electric field. The cations are drawn in the direction of the electric field and the anions in the opposite direction, leading to the relative change in the inter-ionic distance. Depending on the direction of the electric field, the soft spring expands or contracts more than the contraction or expansion of the hard spring in order to maintain the same atomic interaction forces, causing a strain x (a unit cell length change) in proportion to the electric field E . This is the “converse piezoelectric effect”. When expressed as

$$x = d E, \quad (2)$$

the proportionality constant d is called the “piezoelectric constant”.

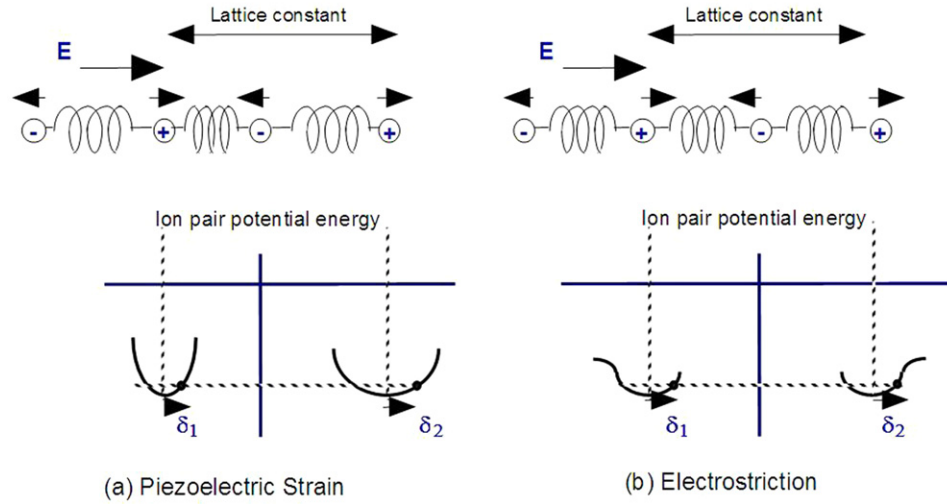


Fig. 3 Microscopic explanation of the piezoestriction (a), and electrostriction (b).

Electrostriction

On the other hand, in Fig. 3(b), the amounts of extension and contraction of the spring are nearly the same, thus the distance between the two cations (lattice parameter) remains almost the same, hence, there is no strain. However, more precisely, ions are not connected by such idealized springs (called “harmonic springs” in which force (F) = spring constant (k) $\times$ displacement (Δ) holds). In most cases, the springs possess “anharmonicity” ($F = k_1\Delta - k_2\Delta^2$), that is, they are somewhat easy to extend but hard to contract. Such subtle differences in the displacement causes a change in the lattice parameter, producing a strain which is independent of the direction of the applied electric field ($+E$ or $-E$), and hence is an even-function of the electric field. This is called the “electrostrictive effect”, and can be expressed as

$$x = M E^2, \quad (3)$$

where M is the “electrostrictive coefficient”.

Note that the 1D asymmetric crystal pictured in Fig. 3(a) also possesses a spontaneous bias of electrical charge, or a “spontaneous dipole moment”. The total dipole moment per unit volume is called the “spontaneous polarization”. When a large reverse bias electric field is applied to a crystal that has a positively aligned spontaneous polarization, another polarization status is formed under a critical field level called “coercive field”, that is another stable crystal state in which the relative positions of the ions are reversed. In terms of an untwinned single crystal, this is equivalent to rotating the crystal 180° about an axis perpendicular to its polar axis. This transition, referred to as “polarization reversal”, also causes a remarkable change in strain. This particular class of substances is referred to as “ferroelectrics”.

Polarization-reorientation related strain

“Polarization reorientation” process or “poling process” in a polycrystalline ferroelectric specimen such as lead zirconate titanate (PZT) is schematically illustrated in Fig. 4. First, the polycrystal is composed of many small single crystals (each is called “grain”) with random crystal orientations. Thus, the complete alignment of the polarization is impossible. Further, due to this crystallographic mis-orientation, some residual stress exists in the specimen, which promotes multi-domain status even under a high electric field. Second, we consider the external electrical field application, started from the initially “negatively poled” status “1”. You can notice some residual domains in each grain. With increasing the electric field up to the “coercive field” E_C “2” (where the free energy at $-P_S$ reaches zero), the largest number of various domains come up to make the total polarization almost zero (i.e., this is the definition of the coercive field). When we further increase the field “3”, the domain rapidly disappears to become close to mono-domain state in each grain. The slope of the strain vs. electric field around “3” corresponds to the intrinsic piezoelectric constant. Third, if we decrease the field now down to the coercive field “4”, we may start to observe some domain generation in grains, then finally at zero field “5”, we observe similar domains in each grain as in the state “1”, though the polarization directions are opposite to the state “1”. We call this state “positively poled”. Generally, what actually observed as a field-induced strain is a complicated combination of the above three basic effects: (1) piezoestriction, (2) electrostriction, and (3) domain-reorientation-related (hysteretic) strain.

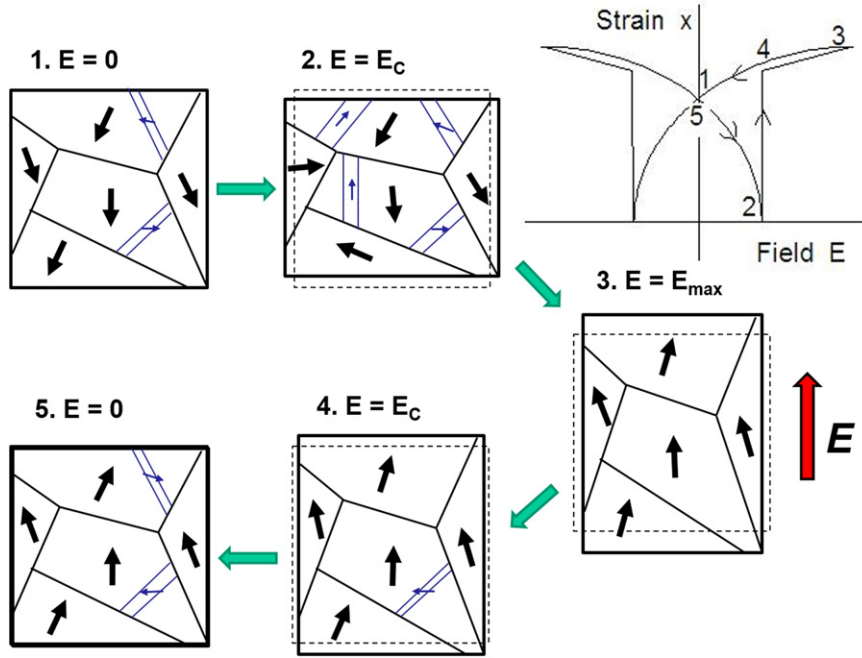


Fig. 4 Domain structure change with the external electric field in polycrystalline ferroelectrics.

Piezoelectric Constitutive Equations and Electromechanical Coupling Factors

Piezoelectric constitutive equations

We consider a practical formula of the Gibbs free energy $G(T, X, E)$ for the case of small value change in external X and E (1D case) under the “isothermal condition”. If the change of parameters is small, we may adopt the two-parameter Taylor expansion approximation up to second derivatives in order to discuss just the linear relationships, based on the description by [Mitsui et al. \(1969\)](#):

$$G(X, E) = G_0 + \left(\frac{\partial G}{\partial X}\right)X + \left(\frac{\partial G}{\partial E}\right)E + \frac{1}{2}\left(\frac{\partial^2 G}{\partial X^2}\right)X^2 + \frac{1}{2}\left(\frac{\partial^2 G}{\partial E^2}\right)E^2 + \left(\frac{\partial^2 G}{\partial X \partial E}\right)XE \quad (4)$$

Taking into account $dG = -SdT - x dX - D dE$ (under $dT = 0$), we obtain first the relations, $\left(\frac{\partial G}{\partial X}\right)_{X,E=0} = -x_0$ and $\left(\frac{\partial G}{\partial E}\right)_{X,E=0} = -D_0$. The values x_0 and D_0 ($\approx P_0$) are considered to be spontaneous strain and spontaneous polarization in the ferroelectric phase of this material, thus we set them as new “origins” in the discussion merely in the ferroelectric phase. Now, [Eq. \(4\)](#) can be transformed as

$$x = -\left(\frac{\partial G(0,0)}{\partial X}\right) = -\left(\frac{\partial^2 G}{\partial X^2}\right)X - \left(\frac{\partial^2 G}{\partial X \partial E}\right)E \quad (5a)$$

$$D = -\left(\frac{\partial G(0,0)}{\partial E}\right) = -\left(\frac{\partial^2 G}{\partial X \partial E}\right)X - \left(\frac{\partial^2 G}{\partial E^2}\right)E \quad (5b)$$

Based on the above linear relationships, we derive the “intensive” parameter-based “piezoelectric constitutive equations”:

$$x = s^E X + dE \quad (6a)$$

$$D = dX + \varepsilon_0 \varepsilon^X E \quad (6b)$$

where the following denotations are used, s^E elastic compliance under constant E , $\varepsilon_0 \varepsilon^X$ dielectric permittivity under stress free:

$$\left\{ \begin{array}{l} s^E = -\left(\frac{\partial^2 G(0,0)}{\partial X^2}\right) \\ \varepsilon_0 \varepsilon^X = -\left(\frac{\partial^2 G(0,0)}{\partial E^2}\right) \\ d = -\left(\frac{\partial^2 G(0,0)}{\partial X \partial E}\right) \end{array} \right\} \quad (7)$$

The Maxwell relation, $\left(\frac{\partial D}{\partial X}\right)_{T,E} = \left(\frac{\partial x}{\partial E}\right)_{T,X}$ verifies that the piezoelectric coefficient d in [Eqs. \(6a\) and \(6b\)](#) are thermodynamically the same.

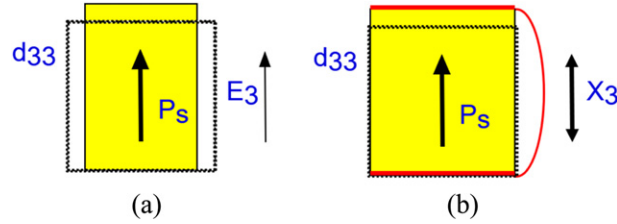


Fig. 5 Calculation models of electro-mechanical coupling factor k for (a) electric input under stress free, and (b) stress input under short-circuit condition.

When we start from the Helmholtz free energy A ($dA = -SdT + Xdx + EdD$), by taking a similar Taylor expansion approach, we obtain another set of piezoelectric constitutive equations in terms of “extensive” parameters, x and D :

$$X = c^D x - h D, \quad (8a)$$

$$E = -h x + \kappa_0 \kappa^x D, \quad (8b)$$

where c^D is elastic stiffness under constant D , and $\kappa_0 \kappa^x$ is inverse permittivity ($\kappa_0 = 1/\epsilon_0$) under strain free condition, and these coefficients are expressed by:

$$\left\{ \begin{array}{l} c^D = \left(\frac{\partial^2 A}{\partial x^2} \right) \\ \kappa_0 \kappa^x = \left(\frac{\partial^2 A}{\partial D^2} \right) \\ h = - \left(\frac{\partial^2 A}{\partial x \partial D} \right) \end{array} \right\} \quad (9)$$

Electromechanical coupling factors

The term, “electromechanical coupling factor” k , is defined as the square value k^2 be the ratio of the converted energy over the input energy: when electric to mechanical

$$k^2 = (\text{Stored mechanical energy} / \text{Input electrical energy}), \quad (10a)$$

or when mechanical to electric,

$$k^2 = (\text{Stored electrical energy} / \text{Input mechanical energy}) \quad (10b)$$

Let us derive Eq. (10a) first practically, when an external electric field E_3 is applied to a piezoelectric material in a pseudo-static process. See Fig. 5(a), when we apply electric field on the top and bottom electrodes under stress free condition ($X = 0$). Input electric energy must be equal to $(1/2)\epsilon_0\epsilon_3^X E_3^2$, and the output strain generated by E_3 should be $d_{33}E_3$. Since the converted/stored mechanical energy is obtained as $(1/2)s_{33}^E x_3^2$, we obtain:

$$\begin{aligned} k_{33}^2 &= [(1/2)(d_{33}E_3)^2 / s_{33}^E] / [(1/2)\epsilon_0\epsilon_3^X E_3^2] \\ &= d_{33}^2 / \epsilon_0\epsilon_3^X s_{33}^E \end{aligned} \quad (11a)$$

Let us now consider Eq. (10b), when an external stress X_3 is applied to a piezoelectric material in a pseudo-static process. Refer to Fig. 5(b). Under short-circuit condition ($E_3 = 0$), the input mechanical energy must be equal to $(1/2)s_{33}^E X_3^2$, and the electric displacement D_3 (or polarization P_3) generated by X_3 should be equal to $d_{33}X_3$ from Eq. (6b). This D_3 can be obtained by integrating the short-circuit current in terms of time through the electric lead. Since the converted/stored electric energy is obtained as $(1/2)\epsilon_0\epsilon_3^X D_3^2$, we obtain:

$$\begin{aligned} k_{33}^2 &= [(1/2\epsilon_0\epsilon_3^X)(d_{33}X_3)^2] / [(1/2)s_{33}^E X_3^2] \\ &= d_{33}^2 / \epsilon_0\epsilon_3^X s_{33}^E \end{aligned} \quad (11b)$$

It is essential to understand that the electromechanical coupling factor k or k^2 (energy transduction or conversion rate) can be exactly the same for both converse (11a) and direct (11b) piezoelectric effects. The conditions under constant X (free stress) or constant E (short-circuit) are considered to be unconstrained.

Constraint physical parameters – Permittivity & elastic compliance

It is important to consider the constraint conditions under which a material will be operated when characterizing the dielectric constant and elastic compliance of that material. When a constant electric field is applied to a piezoelectric sample as illustrated in Fig. 6 Top, the total input electric energy (left) should be equal to a combination of the energies associated with two distinct mechanical conditions that may be applied to the material: (1) stored electric energy under the “mechanically clamped state”, where a constant strain (zero strain) is maintained and the specimen cannot deform, and (2) converted mechanical energy under

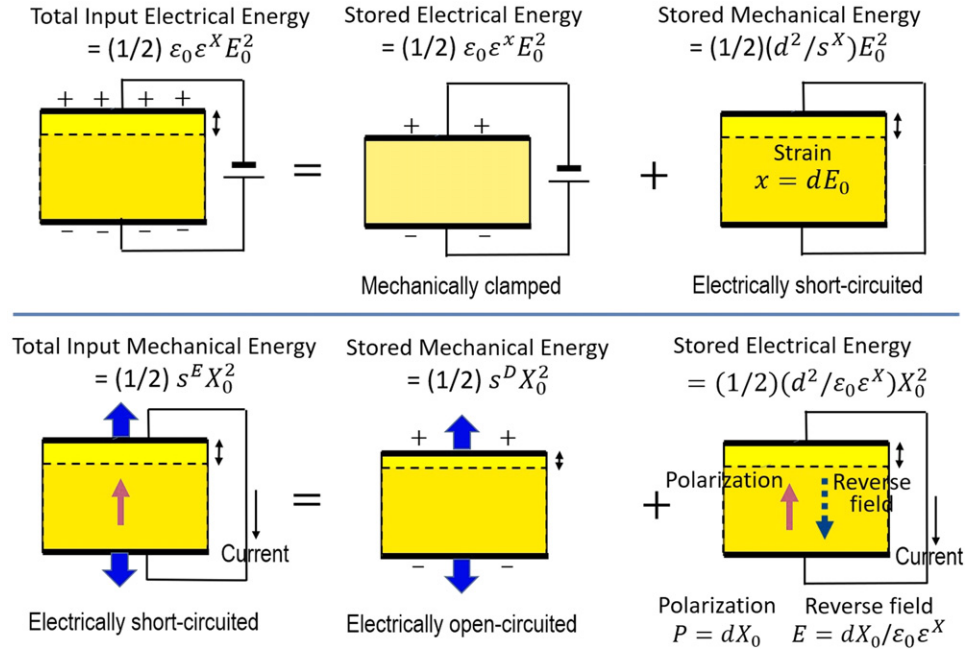


Fig. 6 Schematic representation of the response of a piezoelectric material under: (a) constant applied electric field and (b) constant applied stress conditions.

the “mechanically free state”, in which the material is not constrained and is free to deform. This situation can be expressed (1D case for simplicity) by:

$$\left(\frac{1}{2}\right) \epsilon^X \epsilon_0 E_0^2 = \left(\frac{1}{2}\right) \epsilon^X \epsilon_0 E_0^2 + \left(\frac{1}{2s^E}\right) x^2 = \left(\frac{1}{2}\right) \epsilon^X \epsilon_0 E_0^2 + \left(\frac{1}{2s^E}\right) (dE_0)^2$$

such that:

$$\begin{aligned} \epsilon^X \epsilon_0 &= \epsilon^X \epsilon_0 + \left(\frac{d^2}{s^E}\right) \text{ or} \\ \epsilon^X &= \epsilon^X (1 - k^2) \left[k^2 = \frac{d^2}{\epsilon^X \epsilon_0 s^E} \right] \end{aligned} \quad (12a)$$

When a constant stress is applied to the piezoelectric as illustrated in **Fig. 6 Bottom**, the total mechanical energy will be a combination of (1) stored mechanical energy under the “open-circuit state”, and (2) converted electric energy (i.e., “depolarization field”) under the “short-circuit condition”. This can be expressed as:

$$\left(\frac{1}{2}\right) s^E X_0^2 = \left(\frac{1}{2}\right) s^D X_0^2 + \left(\frac{1}{2}\right) \epsilon^X \epsilon_0 E^2 = \left(\frac{1}{2}\right) s^D X_0^2 + \left(\frac{1}{2}\right) \epsilon^X \epsilon_0 (d / \epsilon_0 \epsilon^X)^2 X_0^2$$

which leads to:

$$s^E = s^D + \left(\frac{d^2}{\epsilon^X \epsilon_0}\right) \text{ or } s^D = s^E (1 - k^2) \left[k^2 = \frac{d^2}{\epsilon^X \epsilon_0 s^E} \right] \quad (12b)$$

In principle, if we measure the permittivity in a piezoelectric specimen under stress-free and completely-clamped conditions, we can obtain ϵ^X and ϵ^x , respectively. Similarly, if we measure the strain in a piezoelectric specimen as a function of applied stress pseudo-statically, under short-circuit and open-circuit conditions, we can obtain s^E and s^D , respectively. Note here that because typical electromechanical coupling factors are $k_{33}^2 = 50\%$ (large!) in popular PZTs, the difference of elastic compliance and permittivity between constraint and unconstraint specimens are significant; that is, doubled difference can be experimentally obtained.

We can also write equations of similar form for the corresponding reciprocal quantities:

$$\begin{cases} \kappa^X / \kappa^x = (1 - k^2) \\ c^E / c^D = (1 - k^2) \end{cases} \left[k^2 = \frac{h^2}{c^D (\kappa_0 \kappa^x)} \right] \quad (13)$$

The above parameter k in **Eq. (13)** is also the “electromechanical coupling factor” in the “extensive” parameter description, and identical to the k in **Eqs. (11a), (11b)**. Note the k expression derivation from the piezoelectric constitutive equations, **Eqs. (6a), (6b), (8a) and (8b)**:

$$k^2 = \frac{(\text{Coupling factor})^2}{(\text{Product of the diagonal parameters})} = \frac{d^2}{s^E \epsilon^X \epsilon_0} = \frac{h^2}{c^D (\kappa_0^X)} [\kappa_0 = 1/\epsilon_0] \quad (14)$$

Figures of Merit in Piezoelectrics

In order to compare the performance superiority of actuator, transducer materials, we usually use a “Figure of Merit (FOM)”. There are five types of important FOM’s for transducers, in particular, piezoelectric materials: (1) the piezoelectric coefficient, d , g , etc., (2) the electromechanical coupling factor, k , energy transmission coefficient, λ , efficiency, η , (3) the mechanical quality factor Q_m , (4) the acoustic impedance Z , and (5) the maximum vibration velocity v_{max} . Each of these quantities are defined in this section.

Piezoelectric Constants

Let us start from the piezoelectric constitutive equations. There are four pairs of description types, depending on the intensive (E , X)/extensive (D , x) parameters:

$$x = s^E X + dE \quad (15a)$$

$$D = dX + \epsilon_0 \epsilon^X E \quad (15b)$$

$$X = c^D x - hD \quad (16a)$$

$$E = -hx + (\kappa^X / \epsilon_0) D \quad (16b)$$

$$x = s^D X + gD \quad (17a)$$

$$E = -gX + (\kappa^X / \epsilon_0) D \quad (17b)$$

$$X = c^E x - eE \quad (18a)$$

$$D = ex + \epsilon_0 \epsilon^X E \quad (18b)$$

An intensive quantity is one whose magnitude is independent of the size of the system, whereas an extensive quantity is one whose magnitude is additive for subsystems (IUPAC definition). In practice, intensive E and X are externally controllable parameters, while extensive D and x are internal material’s parameters. Accordingly, there are four types of piezoelectric coefficients, d , h , g , and e . The magnitude of the strain, x , induced by an applied electric field, E , is characterized by the piezoelectric strain coefficient, d , as:

$$x = (d)E \quad (19)$$

This quantity is an important “FOM for actuators” (Eq. (15a)). The induced electric field, E , is related to the applied stress, X , through the piezoelectric voltage coefficient, g , as:

$$E = (g)X. \quad (20)$$

This quantity is an important “FOM for sensors” (Eq. (17b)). Recall that the direct piezoelectric effect is described by: $P = (d)X$, where P is the induced polarization (almost equal to D for a large permittivity material). When we combine this expression with Eq. (20) we obtain an important relationship between g and d :

$$g = d / \epsilon_0 \epsilon^X \quad (21)$$

where ϵ^X is the dielectric constant/relative permittivity under a free (unclamped) condition.

Eqs. (18a) and (18b) are popularly used for analyzing piezoelectric thin films, where the film strain is constraint/clamped by the substrate (x -constrained). The electric displacement measured via the short-circuit current by changing the strain via the substrate bending can provide the piezoelectric e constant, which is related as:

$$e = d / s^E \quad (22)$$

where s^E is the elastic compliance under a short-circuit condition. Finally, h is basically an inverse component of the d tensor (like $1/d$).

Electromechanical Coupling Factor k and Related Coefficients

The terms, electromechanical coupling factor, energy transmission coefficient, and efficiency are sometimes confused. All are related to the conversion rate between electrical energy and mechanical energy, but their definitions are different.

The electromechanical coupling factor k

The piezoelectric can transduce the input electric energy to the output mechanical energy, and vice versa. Thus, we introduce in the previous section the electromechanical coupling factor k , which corresponds to the rate of electromechanical transduction.

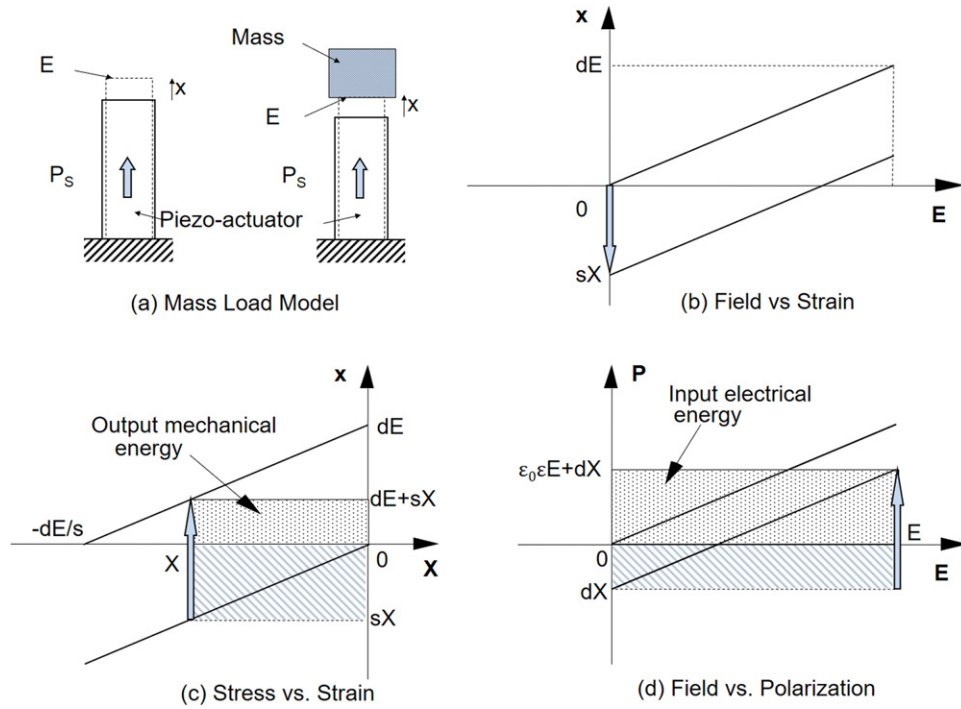


Fig. 7 Calculation of the input electrical and output mechanical energy: (a) load mass model for the calculation, (b) electric field versus induced strain curve, (c) stress versus strain curve, and (d) electric field versus polarization curve.

The internal energy U of a piezoelectric is given by summation of the mechanical energy $U_M (= \int x dX)$ and the electrical energy $U_E (= \int D dE)$. U is calculated as follows, when linear relations Eqs. (6a) and (6b) are applicable:

$$\begin{aligned}
 U &= U_M + U_E \\
 &= [(1/2) \sum_{i,j} s_{ij}^E X_j X_i + (1/2) \sum_{m,i} d_{mi} E_m X_i] \\
 &\quad + [(1/2) \sum_{m,i} d_{mi} X_i E_m + (1/2) \sum_{k,m} \epsilon_0 \epsilon_{mk}^X E_k E_m] \\
 &= U_{MM} + 2U_{ME} + U_{EE} \\
 &= (1/2) \sum_{i,j} s_{ij}^E X_j X_i + 2 \cdot (1/2) \sum_{m,i} d_{mi} E_m X_i + (1/2) \sum_{k,m} \epsilon_0 \epsilon_{mk}^X E_k E_m.
 \end{aligned} \tag{23}$$

The s and ϵ terms represent purely mechanical and electrical energies (U_{MM} and U_{EE}), respectively, and the d term denotes the energy transduced from electrical to mechanical energy or vice versa through the piezoelectric effect (U_{ME}). The electromechanical coupling factor k is also defined by:

$$k = U_{ME} / \sqrt{U_{MM} U_{EE}}. \tag{24}$$

From Eq. (23), we obtain

$$\begin{aligned}
 k^2 &= \left[\left(\frac{1}{2} \right) dEX \right]^2 / \left[\left(\frac{1}{2} \right) s^E X^2 \right] \left[\left(\frac{1}{2} \right) \epsilon_0 \epsilon^X E^2 \right] \\
 &= d^2 / \epsilon_0 \epsilon^X s^E.
 \end{aligned} \tag{25}$$

Note that the final expressions Eq. (25) gives exactly the same as Eqs. (11a) and (11b).

The energy transmission coefficient λ_{max}

Not all the stored energy can actually be used, and the actual work done depends on the mechanical load. Recall the mechanical work is represented by force $F \times$ distance x ; with zero mechanical load or a complete clamp (no strain), no output work is done. The energy transmission coefficient is defined by

$$\lambda_{max} = (\text{Output mechanical energy} / \text{Input electrical energy})_{max} \tag{26a}$$

$$\lambda_{max} = (\text{Output electrical energy} / \text{Input mechanical energy})_{max} \tag{26b}$$

The difference of the above Eqs. (26a) and (26b) from Eqs. (10a) and (10b) is “stored” or “output/spent”.

Let us consider the case where an electric field E is applied to a piezoelectric under constant external stress X (< 0 , because a compressive stress is necessary to work to the outside). This corresponds to the situation that a mass is put suddenly on the actuator, as shown in Fig. 7(a). Fig. 7(b) shows two electric-field versus induced-strain curves, corresponding to two conditions;

under the mass load and no mass. Because the area on the field-strain domain does not mean the energy, we should use the stress-strain and field-polarization domains in order to discuss the mechanical and electrical energy, respectively [Recall the situation in Eq. (23)]. Fig. 7(c) illustrates how to calculate the mechanical energy. Note that the mass shrinks the actuator first by sX (s : piezomaterial's compliance, and $X < 0$). This mechanical energy sX^2 is a sort of "loan" of the actuator credited from the mass, which should be subtracted later. This energy corresponds to the hatched area in Fig. 7(c). By applying the step electric field, the actuator expands by the strain level dE under a constant stress condition. This is the mechanical energy provided from the actuator to the mass, which corresponds to dEX . Like paying back the initial "loan", the output work (from the actuator to the mass) can be calculated as the area subtraction (shown by the dotted area in Fig. 7(c))

$$\int (-X)dx = -(dE + sX)X. \quad (27)$$

Fig. 7(d) illustrates how to calculate the electrical energy. The mass load X generates the "loan" electrical energy by inducing $P = dX$ (see the hatched area in Fig. 5(d)). By applying a sudden electric field E , the actuator (like a capacitor) receives the electrical energy of $\epsilon_0 \epsilon E^2$. Thus, the total energy is given by the area subtraction (shown by the dotted area in Fig. 7(d))

$$\int (E)dP = (\epsilon_0 \epsilon E + dX)E. \quad (28)$$

We need to choose a proper load to maximize the energy transmission coefficient. From the maximum condition of

$$\begin{aligned} \lambda &= -x \cdot X/P \cdot E = X \int (-X)dx/E \int (E)dP \\ &= -[d(X/E) + s(X/E)^2]/[\epsilon_0 \epsilon + d(X/E)] \end{aligned} \quad (29)$$

Letting X/E , then.

$$\lambda = -(sy^2 + dy)/(dy + \epsilon_0 \epsilon).$$

The maximum λ can be obtained when y satisfies.

$$(d\lambda/dy) = 0 = [-(2sy + d) \cdot (dy + \epsilon_0 \epsilon) + (sy^2 + dy) \cdot d]/(dy + \epsilon_0 \epsilon)^2.$$

Then, from

$$y_0^2 + 2(\epsilon_0 \epsilon/d)y_0 + (\epsilon_0 \epsilon/s) = 0,$$

$$y_0 = (\epsilon_0 \epsilon/d) \left[-1 + \sqrt{1 - k^2} \right].$$

Here, $k^2 = d^2/(s \cdot \epsilon_0 \epsilon)$. Note that only $y_0 = (\epsilon_0 \epsilon/d) \left[-1 + \sqrt{1 - k^2} \right]$ is valid for realizing the meaningful maximum point, since $y_0 = (\epsilon_0 \epsilon/d) \left[-1 - \sqrt{1 - k^2} \right]$ and $y_0 = (\epsilon_0 \epsilon/d) \left[-1 + \sqrt{1 - k^2} \right]$ provide $(d^2\lambda/dy^2) > 0$ (i.e., minimum point) and < 0 (i.e., maximum point), respectively.

By putting $y = y_0$ into $\lambda(y)$, we can get the maximum value of λ :

$$\lambda_{max} = -s[-2(\epsilon_0 \epsilon/d)y_0 - (\epsilon_0 \epsilon/s)] + dy_0)/(dy_0 + \epsilon_0 \epsilon)$$

we can finally obtain the following two equivalent expressions:

$$\lambda_{max} = [(1/k) - \sqrt{1/k^2 - 1}]^2 = [(1/k) + \sqrt{1/k^2 - 1}]^{-2} \quad (30)$$

Notice that $k^2/4 < \lambda_{max} < k^2/2$ for a reasonable k value ($< 90\%$). For a small k , $\lambda_{max} = k^2/4$, and for a large k , $\lambda_{max} = k^2/2$.

It is also worth noting that the maximum condition stated above does not agree with the condition which provides the maximum output mechanical energy. The maximum output energy can be obtained when the dotted area in Fig. 7(c) becomes maximum under the constraint of the rectangular corner point tracing on the line (from dE on the vertical axis to $-dE/s$ on the horizontal axis). Therefore, the load should be a half of the maximum generative stress and the mechanical energy: $-[dE - s(dE/2s)](-dE/2s) = (dE)^2/4s$. In this case, since the input electrical energy is given by $[\epsilon_0 \epsilon E + d(-dE/2s)] E$,

$$\lambda = 1/2[(2/k^2) - 1], \quad (31)$$

which is close to the value λ_{max} when k is small, but has a difference when k is large, as predicted.

The efficiency η

$$\eta = (\text{Output mechanical energy})/(\text{Consumed electrical energy}) \quad (32a)$$

$$\eta = (\text{Output electrical energy})/(\text{Consumed mechanical energy}). \quad (32b)$$

The difference of the efficiency definition from Eqs. (26a) and (26b) is "input" energy and "consumed" energy in the denominators. In a work cycle (e.g., an electric field cycle), the input electrical energy is transformed partially into mechanical

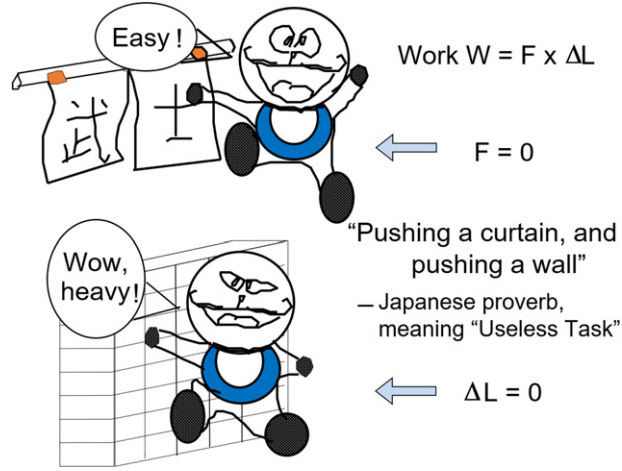


Fig. 8 Concept of mechanical impedance matching.

energy and the remaining is stored as electrical energy (electrostatic energy like a capacitor, called “damped capacitance”) in an actuator. In this way, the ineffective electrostatic energy can be returned to the power source, leading to near 100% efficiency, if the loss is small. Since typical values of dielectric loss in PZT are about 1%–3%, the practical efficiency η should reach up to 97%–99%.

Mechanical Quality Factor Q_M

The mechanical quality factor, Q_M , is a parameter that characterizes the sharpness of the electromechanical resonance spectrum. When the motional admittance Y_m is plotted around the resonance frequency ω_0 , the mechanical quality factor Q_M is defined with respect to the full width $[2\Delta\omega]$ at $Y_m/\sqrt{2}$ as:

$$Q_M = \omega_0 / 2\Delta\omega. \quad (33)$$

Also note that Q_M^{-1} is equal to the mechanical loss ($\tan \phi$) [i.e., microscopic origin]. When we define a complex elastic compliance, $s^E = s^{E'} - j s^{E''}$, the mechanical loss tangent is provided by $\tan \phi = s^{E''}/s^{E'}$. The Q_M value is very important in evaluating the magnitude of the resonant displacement and strain. The vibration amplitude at an off-resonance frequency ($dE \cdot L$, L : length of the sample) is amplified by a factor proportional to Q_M at the resonance frequency. For example, a longitudinally vibrating rectangular plate through the transverse piezoelectric effect d_{31} generates the maximum displacement given by $(8/\pi^2) Q_M d_{31} E L$. The mechanical quality factor Q_M at the antiresonance frequency will be discussed in Section “Piezoelectric Resonance and Antiresonance”.

Acoustic Impedance Z

Though this parameter is not unique for piezoelectrics, it is closely associated with the piezoelectric device designing. The acoustic impedance Z is a parameter used for evaluating the acoustic energy transfer between two materials. It is defined, in general, by $Z^2 = (\text{pressure}/\text{volume velocity})$, which is translated in a solid material as

$$Z = \sqrt{\rho c}, \quad (34)$$

where ρ is the density and c is the elastic stiffness of the material.

Acoustic impedance (or mechanical impedance) matching is necessary for transferring mechanical energy from one material to the other. **Fig. 8** shows a conceptual cartoon illustrating two extreme cases. The mechanical work done by one material on the other is evaluated by the product of the applied force F and the displacement ΔL :

$$W = F \times \Delta L \quad (35)$$

If the material is very soft, the force F can be very small, leading to very small W (practically no work!). This corresponds to “Pushing a curtain,” exemplified by the case when the acoustic wave is generated in water directly by a hard PZT transducer. Most of the acoustic energy generated in the PZT is reflected at the interface, and only a small portion of acoustic energy transfers into water. On the other hand, if the material is very hard, the displacement ΔL will be very small, again leading to very small W . This corresponds to “Pushing a wall.” Polymer piezoelectric PVDF (polyvinylidene di-fluoride) cannot drive a hard steel part efficiently. Therefore, the acoustic impedance must be adjusted to maximize the output mechanical power:

$$\sqrt{\rho_1 c_1} = \sqrt{\rho_2 c_2}, \quad (36)$$

where ρ is the density and c is the elastic stiffness, and the subscripts 1 and 2 denote the two materials. In practice, acoustic impedance matching layers (Elastically intermediate materials between PZT and water, such as a polymer. More precisely the

acoustic impedance Z should be the geometrical average $\sqrt{Z_1 \cdot Z_2}$.) are fabricated on the PZT transducer to optimize the transfer of mechanical energy to water.

In more advanced discussions, there are three kinds of impedances; specific acoustic impedance (pressure/particle speed), acoustic impedance (pressure/volume speed) and radiation impedance (force/speed). See Ref. [Kinsler et al. \(1982\)](#) for the details.

Maximum Vibration Velocity v_{max}

The power density of a piezoelectric is measured by different figures of merit (FOM) for different applications ([Uchino, 2020](#)):

- (1) Off-Resonance Actuator Applications – Positioners
FOM = d (piezoelectric constant)
- (2) Resonance Actuator Applications – Ultrasonic Motors
FOM = v (vibration velocity) $\approx Q_m \cdot d$ (for low level excitation)
- (3) Resonance transducer applications – piezoelectric transformers, sonars (transmitters & receivers)

FOM = $k \cdot v$ (k : electromechanical coupling factor).

In order to obtain a large mechanical output power, the ceramics are driven under a high vibration level, namely under a relatively large AC electric field around the electromechanical resonance frequency. Though the “vibration velocity” (i.e., first derivative of the vibration displacement in respect of time) is almost proportional to the applied AC electric field under relatively small field range, with increasing the electric field, the induced vibration velocity will saturate above a certain critical field. This is originated from the sudden intensive elastic loss increase, or the reduction of the mechanical quality factor above this critical field. And, heat generation becomes significant, as well as a degradation in piezoelectric properties. Therefore, the high-power device such as an ultrasonic motor requires a very ‘hard’ piezoelectric with a high mechanical quality factor Q_m (i.e., low elastic loss) in order to suppress heat generation. The Q_m is defined as an inverse value of the intensive elastic loss factor, $\tan \phi'$. It is also notable that the actual mechanical vibration velocity at the resonance frequency is directly proportional to this Q_m value (i.e., displacement amplification factor).

In order to analyze the various piezoelectric parameter changes as a function of vibration level, we occasionally use vibration velocity, instead of the applied electric field. Though the vibration amplitude may be used, the vibration velocity is used more popularly in the discussion. The reason is to eliminate the size effect; that is, when the vibration amplitude is small and proportional to the applied electric field and the length L , it should be expressed by

$$\Delta L = (8/\pi^2) Q_m d_{31} E_3 \sin(\omega_R t) \quad (37)$$

for a d_{31} type rectangular piezoelectric plate [Refer to Section “Piezoelectric Resonance and Antiresonance” for the derivation]. Since the vibration velocity at the edge of the plate sample is the first derivative of amplitude in respect of t , we obtain $v = (8/\pi^2) \cdot Q_m d_{31} L E_3 \omega_R \cos(\omega_R t)$. Taking into account the fundamental resonance frequency $f_R = (1/\sqrt{\rho s_{11}})/2L$, the vibration velocity at the plate edge can be transformed as

$$v = (8/\pi) Q_m d_{31} E_3 (1/\sqrt{\rho s_{11}}) \cos(\omega_R t). \quad (38)$$

Note that the vibration amplitude is the sample-size L dependent, but that the “vibration velocity” is not. Because the vibration velocity is proportional to the electric field, and the proportional constant is given primarily by $Q_m d_{31}/\sqrt{\rho s_{11}} = Q_m d_{31} v_{11}$, which is a material’s constant, we use it as a measure of the vibration level.

As explained above, with increasing the electric field, the induced vibration velocity will saturate above a certain critical field, and heat generation is associated. Since the additional electric power is converted mostly to heat, rather than the vibration velocity increase, we define the “maximum vibration velocity” as the v_{max} under which the piezoelectric plate shows 20°C temperature rise at the nodal point (i.e., the specimen center part) above the room temperature. The RMS (root mean square) value of v_{max} of popular hard PZT rectangular plates ranges from 0.3 m/s to 0.6 m/s, which is a sort of material’s constant, important parameter for the high-power applications. When we consider the high-power performance in a wide variety of piezo-materials such as Pb-free and PZT, the “maximum mechanical energy density” is more suitable by taking into account the mass density, which is defined as $(1/2)\rho v_{rms}^2$ under the maximum vibration velocity condition. Current top data ranges from 1000 to 1500 J/m³. By multiplying the resonance frequency f on the mechanical energy density, we can obtain the maximum vibration power density, the top data of which ranges 30 W/cm³.

Piezoelectric Resonance and Antiresonance

When the field E is alternating, mechanical vibration is caused in a piezoelectric specimen. If the drive frequency is adjusted to its mechanical resonance frequency of the piezoelectric specimen, the vibrating displacement is significantly amplified. This phenomenon can be understood as a strain amplification due to synchronous accumulation of the input electric energy with time (“amplification in terms of time”), which is called “piezoelectric resonance”. The amplification factor is proportional to the mechanical quality factor Q_M (inversely proportional to the elastic loss). Piezoelectric resonance is very useful for realizing energy trap devices, filters, actuators, medical and underwater transducers, piezo-transformers etc. We consider in this section the electromechanical resonance under an AC external electric field theoretically. The simplest specimen geometry k_{31} type is discussed to learn the difference between resonance and antiresonance vibration modes intuitively. We also introduce the difference of the

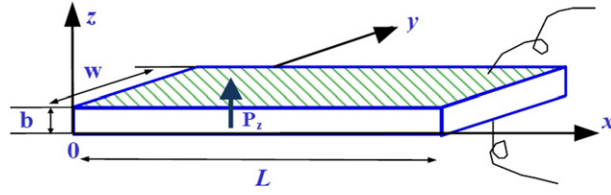


Fig. 9 Longitudinal vibration through the transverse piezoelectric effect (d_{31}) in a rectangular plate ($L \gg w \gg b$).

“mechanical quality factor” Q_m at the resonance and antiresonance frequencies by integrating three losses (i.e., dielectric, elastic and piezoelectric losses).

Longitudinal Vibration Analysis – k_{31} Type

Let us consider the longitudinal mechanical vibration of a piezoceramic plate through the transverse piezoelectric effect (d_{31}), as shown in **Fig. 9**. Sinusoidal electric field E_z (angular frequency ω) is applied along the polarization P_z direction. If the polarization is in the z -direction and x - y top and bottom planes are the planes of the electrodes, the extensional vibration in the x (length) direction is represented by the following dynamic equations (when the length L is more than 4–6 times of the width w or the thickness b , we can neglect the coupling modes with width or thickness vibrations):

$$\rho(\partial^2 u / \partial t^2) = F = (\partial X_{11} / \partial x) + (\partial X_{12} / \partial y) + (\partial X_{13} / \partial z), \quad (39)$$

where ρ is the density of the piezo-ceramic, u is the displacement of a small volume element in the ceramic plate in the x -direction.

We integrate the following piezoelectric constitutive equations (1-D expression) into the dynamic equation:

- (1) $D = \epsilon_0 \epsilon^X E + d X$ and
- (2) $x = d E + s^E X$,

where electric displacement D and strain x are controlled by the intensive parameters, electric field E and stress X . First, the strain, displacement dynamic modes are obtained from the above constitutive second equation. The relations between stress, electric field (only E_z exists) and the induced strain in 3-D expression are given by:

$$\begin{aligned} x_1 &= s_{11}^E X_1 + s_{12}^E X_2 + s_{13}^E X_3 + d_{31} E_3, \\ x_2 &= s_{12}^E X_1 + s_{11}^E X_2 + s_{13}^E X_3 + d_{31} E_3, \\ x_3 &= s_{13}^E X_1 + s_{13}^E X_2 + s_{33}^E X_3 + d_{33} E_3, \\ x_4 &= s_{44}^E X_4, \\ x_5 &= s_{44}^E X_5, \\ x_6 &= 2(s_{11}^E - s_{12}^E) X_6. \end{aligned} \quad (40)$$

Note $s_{66} = 2(s_{11} - s_{12})$ in the ∞mm symmetry like electrically-poled ceramics.

When the plate is very long and thin, X_2 and X_3 may be set equal to zero through the plate. Since shear stress will not be generated by the electric field E_z ($= E_3$), **Eq. (40)** is reduced to only one equation:

$$x_1 = s_{11}^E X_1 + d_{31} E_3, \text{ or } X_1 = x_1 / s_{11}^E - (d_{31} / s_{11}^E) E_z. \quad (41)$$

Under AC electric field E_z at an angular frequency ω , we introduce **Eq. (41)** into **Eq. (39)**. Then, knowing strain definition $x_1 = \partial u / \partial x$ (non-suffix x corresponds to the Cartesian coordinate, and x_1 is the strain along the 1-axis (or x -direction) and $\partial E_z / \partial x = 0$ (due to the equal potential on both top and bottom electrodes), we obtain the following “harmonic vibration equation”:

$$\begin{aligned} \rho(\partial^2 u / \partial t^2) &= (1 / s_{11}^E) (\partial x_1 / \partial x), \\ &= \omega^2 \rho s_{11}^E u = \partial^2 u / \partial x^2. \end{aligned} \quad (42)$$

Here, ω is the drive frequency and u is the x -axis displacement. Supposing the displacement u also vibrates with the frequency of ω , a general solution $u = u_1(x)e^{j\omega t} + u_2(x)e^{-j\omega t}$ is substituted into **Eq. (42)**, and with the boundary condition $X_1 = 0$ at $x = 0$ and L (sample length) (due to the mechanically-free condition at the plate end), the following solution can be obtained:

$$\begin{aligned} (\text{strain}) \quad \partial u / \partial x = x_1 &= d_{31} E_z [\sin \omega(L - x) / v + \sin(\omega x / v)] / \sin(\omega L / v) \\ &= d_{31} E_z \left(\frac{\cos \left[\frac{\omega(L - 2x)}{2v} \right]}{\cos \left(\frac{\omega L}{2v} \right)} \right) \end{aligned} \quad (43)$$

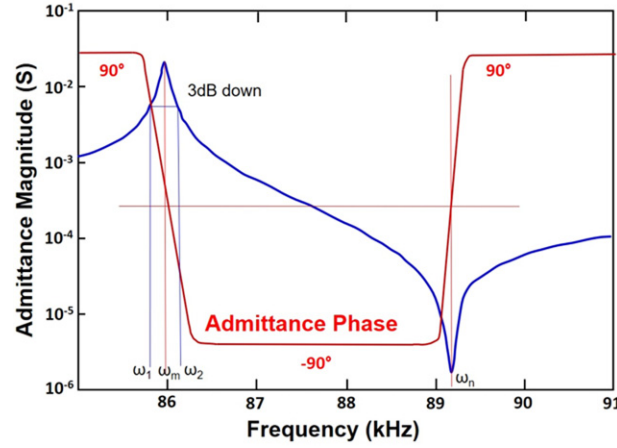


Fig. 10 Admittance spectrum of the k_{31} rectangular plate around its resonance and antiresonance frequencies. ($L = 20$ mm).

$$(\text{total displacement}) \Delta L = \int_0^L x_1 dx = d_{31} E_z L (2\nu/\omega L) \tan(\omega L/2\nu). \quad (44)$$

Here, ν is the “sound velocity” in the piezo-ceramic which is expressed by

$$\nu_{11}^E = 1/\sqrt{\rho s_{11}^E}. \quad (45)$$

The strain distribution in Eq. (43) is symmetrically sinusoidal in respect of $x = L/2$ position, and the maximum strain (i.e., nodal line) exists on this line. Note that $\omega \rightarrow 0$ (i.e., pseudo-DC) makes Eq. (43) to $x_1 = d_{31} E_z$; that is, uniform strain distribution on the piezo-plate.

Admittance Around Resonance and Antiresonance

When the specimen is utilized as an electrical component such as a filter or a vibrator, the electrical admittance [defined by (induced current)/(applied voltage) ratio] or impedance [(applied voltage)/(induced current)] plays an important role. Now we use the first piezoelectric constitutive equation $D = \epsilon_0 \epsilon^X E + d X$. The current flow into the specimen is described by the surface charge increment, $\partial D_3/\partial t$. Though the electric field is uniform in the sample due to the surface electrode, the electric displacement D is not uniform because of the stress X distribution, maximum at the nodal line ($x = L/2$). The total current is given by:

$$\begin{aligned} i &= j\omega w = \int_0^L D_3 dx = j\omega w \int_0^L (d_{31} x_1 + \epsilon_0 \epsilon_{33}^X E_z) dx \\ &= j\omega w \int_0^L [d_{31} \{x_1/s_{11}^E - (d_{31}/s_{11}^E) E_z\} + \epsilon_0 \epsilon_{33}^X E_z] dx, \end{aligned} \quad (46)$$

where w is the plate width. Note that the above current is internal “displacement current” in the piezo-specimen. Thus, the externally measuring current should be $(-i)$. Also $E_z = -\text{grad}(V)$. Using strain distribution in Eq. (43), the admittance for the mechanically free sample is calculated to be:

$$\begin{aligned} Y &= (i_{out}/V) = (-i_{in}/-E_z b) \\ &= (j\omega w L/E_z b) \int_0^L \left[(d_{31}^2/s_{11}^E) \left(\frac{\cos\left[\frac{\omega(L-2x)}{2\nu_{11}^E}\right]}{\cos\left(\frac{\omega L}{2\nu_{11}^E}\right)} \right) E_z + [\epsilon_0 \epsilon_{33}^X - (d_{31}^2/s_{11}^E)] E_z \right] dx \\ &= (j\omega w L/b) \epsilon_0 \epsilon_{33}^{LC} [1 + (d_{31}^2/\epsilon_0 \epsilon_{33}^{LC} s_{11}^E) (\tan(\omega L/2\nu_{11}^E)/(\omega L/2\nu_{11}^E))], \end{aligned} \quad (47)$$

where the sound velocity of the piezoelectric specimen ν_{11}^E is given by Eq. (45), w , L and b are the width, length, and thickness of the rectangular piezo-sample, and V is the applied voltage ($= -E_z \cdot b$).

ϵ_{33}^{LC} is the permittivity in a “longitudinally clamped” (LC) specimen, which is given by.

$$\begin{aligned} \epsilon_{33}^{LC} &= \epsilon_0 \epsilon_{33}^X - (d_{31}^2/s_{11}^E), \quad \text{or} \\ &= \epsilon_0 \epsilon_{33}^X (1 - k_{31}^2). \quad (k_{31}^2 = d_{31}^2/\epsilon_0 \epsilon_{33}^X s_{11}^E) \end{aligned} \quad (48)$$

Note here that this ϵ_{33}^{LC} is different from extensive permittivity ϵ_{33}^X , precisely speaking. ϵ_{33}^{LC} is the permittivity of the specimen mechanically-clamped only along the x (or 1, length) direction, free along z (or 3, polarization direction) or y directions; while ϵ_{33}^X

means the permittivity clamped completely in the three directions. The first term $(j\omega wL/b)\epsilon_0\epsilon_{33}^{LC}$ of admittance Eq. (47) is the “damped capacitance” (longitudinally clamped), and the second term is characterized by $\tan(\omega L/2v)$, which changes from 0, though $+\infty$, to $-\infty$ with ω (neglecting the elastic loss), originated from capacitance change with the mechanical vibration (i.e., “motional capacitance”). Fig. 10 shows an example admittance magnitude and phase spectra for a rectangular piezo-ceramic plate ($L = 20$) around a fundamental longitudinal mode (k_{31}) frequency through the transverse piezoelectric effect (d_{31}) on the basis of Eq. (47). Note that the shown data include losses (Refer to Eq. (54) with losses), and the 3 dB down method to obtain mechanical quality factor Q_m is also inserted in advance.

The piezoelectric resonance is achieved where the admittance becomes infinite or the impedance is zero (neglecting elastic loss). The resonance frequency f_R is calculated from Eq. (47) (by putting $\omega L/2v = \pi/2$ for infinite admittance $\tan(\omega L/2v) = \infty$), and the fundamental frequency is given by

$$f_R = \omega_R/2\pi = v_{11}^E/2L = 1/(2L\sqrt{\rho s_{11}^E}), \quad (49)$$

which indicates that the resonance frequency of the k_{31} mode corresponds to the primary mechanical resonance directly expressed by a half wavelength on the piezoelectric specimen of length L . On the other hand, the antiresonance state is generated for zero admittance or infinite impedance:

$$(\omega_A L/2v) \cot(\omega_A L/2v) = -d_{31}^2/\epsilon_{33}^{LC} s_{11}^E = -k_{31}^2/(1 - k_{31}^2). \quad (50)$$

which indicates that the antiresonance frequency of the k_{31} mode corresponds to the subsidiary mechanical resonance originated from the electromechanical coupling factor. By the way, the final transformation of Eq. (50) used the definition,

$$k_{31} = d_{31}/\sqrt{s_{11}^E \epsilon_{33}^{LC}}. \quad (51)$$

If we approximate the antiresonance frequency for a small k_{31}^2 (such that $|k_{31}| < 30\%$), we obtain

$$f_A = \omega_A/2\pi = f_R \left(1 + \frac{4}{\pi^2} k_{31}^2\right), \quad (52)$$

which exhibits the subsidiary resonance correlated with the electromechanical coupling factor clearly, and f_A is slightly higher than f_R (4% for $|k_{31}| = 30\%$). Though we skip the k_{33} mode, the situation is rather different (opposite) from the above k_{31} case. Refer to Ref. Uchino (2020) for further discussion.

Now we expand the resonance/antiresonance dynamic equations by integrating dielectric, elastic and piezoelectric losses. We introduce the “complex parameters” into the admittance formula Eq. (47) (Uchino, 2020):

$$\begin{cases} \epsilon_{33}^{X*} = \epsilon_{33}^X (1 - j \cdot \tan\delta'_{33}) \\ s_{11}^{E*} = s_{11}^E (1 - j \cdot \tan\phi'_{11}) \\ d_{31}^* = d_{31} (1 - j \cdot \tan\theta'_{31}) \end{cases} \quad (53)$$

where $\tan\delta'_{33}$, $\tan\phi'_{11}$ and $\tan\theta'_{31}$ are “intensive” dielectric, elastic and piezoelectric loss factors.

$$Y = Y_d + Y_m = j\omega C_d (1 - j \tan\delta_{33}''') + j\omega C_d K_{31}^2 [(1 - j(2 \tan\theta_{31}' - \tan\phi_{11}'))][(\tan(\omega L/2v_{11}^{E*})/(\omega L/2v_{11}^{E*}))] \quad (54)$$

where the following notations are adopted:

$$C_0 = (wL/b)\epsilon_0\epsilon_{33}^{X*} \text{ (free electrostatic capacitance, real number)} \quad (55)$$

$$C_d = (1 - k_{31}^2)C_0 \text{ (damped/clamped capacitance, real number)} \quad (56)$$

$$K_{31}^2 = \frac{k_{31}^2}{1 - k_{31}^2} \quad (57)$$

Note that the loss for the first term (‘damped/clamped’ admittance) is represented by the dielectric loss $\tan\delta'''$:

$$\tan\delta_{33}''' = [1/(1 - k_{31}^2)][\tan\delta_{33}' + k_{31}^2(\tan\phi_{11}' - 2 \tan\theta_{31}')] \quad (58)$$

Though the formula $\tan\delta_{33}'''$ is similar to the “extensive” non-prime loss $\tan\delta$, because the extensive loss should be under 3D clamped condition, not under just 1D longitudinally clamped as in the k_{31} case. Taking into account

$$v_{11}^{E*} = \frac{1}{\sqrt{\rho s_{11}^E (1 - j \tan\phi_{11}')}} = v_{11}^E \left(1 + j \frac{\tan\phi_{11}'}{2}\right), \quad (59)$$

we further calculate $1/[\tan(\omega L/2v^*)]$ with an expansion-series approximation around the A-type resonance frequency ($\omega_A L/2v = \pi/2$). [“A-type” and “B-type” resonances are alternatively used for the “resonance” and “antiresonance” conventionally.] Taking into account that the resonance state is defined in this case for the minimum impedance point, and using new frequency parameters,

$$\Omega_A = \omega_A L/2v_{11}^E = \pi/2, \Delta\Omega_A = \Omega - \pi/2 (< 1), \quad (60)$$

with the relationship around the A-type resonance frequency

$$\frac{1}{\tan\Omega^*} = \cot\left(\frac{\pi}{2} + \Delta\Omega_A - j\frac{\pi}{4} \tan\phi_{11}'\right) = \Delta\Omega_A - j\frac{\pi}{4} \tan\phi_{11}',$$

the motional admittance Y_m (by neglecting Y_d because of the magnitude difference) is approximated around the first resonance frequency ω_A by

$$Y_m = j(8/\pi^2)\omega_A C_d K_{31}^2 [(1 - j(2\tan\theta'_{31} - \tan\phi'_{11}))]/[(4/\pi)\Delta\Omega_A - j\tan\phi'_{11}]. \quad (61)$$

The maximum Y_m is obtained at $\Delta\Omega_A = 0$:

$$Y_m^{max} = (8/\pi^2)\omega_A C_d K_{31}^2 (\tan\phi'_{11})^{-1} = (8/\pi^2)\omega_A C_0 k_{31}^2 Q_A, \quad (62)$$

The mechanical quality factor for A-type resonance $Q_A = (\tan\phi'_{11})^{-1}$ can be proved as follows: Q_A is defined by $Q_A = \omega_A/2\Delta\omega$, where $2\Delta\omega$ is a full width of the 3 dB down (i.e., $1/\sqrt{2}$, because $20\log_{10}(1/\sqrt{2}) = -3.01$) of the maximum value Y_m^{max} at ω_A . Refer to Fig. 10. Since $|Y| = |Y_m^{max}|/\sqrt{2}$ can be obtained when the 'conductance = susceptance'; $\Delta\Omega_A = (\pi/4)\tan\phi'_{11}$ [see the denominator of Eq. (61)],

$$Q_A = \Omega_A/2\Delta\Omega_A = (\pi/2)/2(\pi/4)\tan\phi'_{11} = (\tan\phi'_{11})^{-1}. \quad (63)$$

Similarly, the maximum displacement u^{max} is obtained at $\Delta\Omega = 0$:

$$u^{max} = (8/\pi^2)d_{31}E_Z L Q_A. \quad (64)$$

The maximum displacement at the resonance frequency is $(8/\pi^2)Q_A$ times larger than that at a non-resonance frequency, $d_{31}E_Z L$. Under the constant voltage/field drive, the displacement is amplified at the resonance frequency, while under the constant current drive, the displacement u and the impedance Z are amplified at the antiresonance frequency by the factor of $(8/\pi^2)Q_B$, as explained below.

On the other hand, a higher quality factor at the antiresonance is usually observed in comparison with that at the resonance point (Hirose *et al.*, 1996a; Mezheritsky, 2002) in most of Pb-based piezo-ceramics, the reason of which was interpreted by Mezheritsky from the combination of three loss factors (Mezheritsky, 2002). In this manuscript, we introduce our user-friendly formula to determine piezoelectric losses by analyzing the admittance/impedance spectra at resonance and antiresonance (Zhuang *et al.*, 2009). The antiresonance corresponds to the minimum admittance of Eq. (47):

$$\begin{aligned} Y &= (j\omega L/b)\epsilon_0\epsilon_{33}^X [(1 - k^2) + k^2\tan(\omega L/2v_{11}^E)/(\omega L/2v_{11}^E)], (v_{11}^E = 1/\sqrt{\rho s_{11}^E}) \\ &= j\omega C_0 \left[(1 - k_{31}^2) + k_{31}^2 \frac{\tan(\Omega_{11})}{\Omega_{11}} \right] \end{aligned}$$

Here, $v_{11}^E = 1/\sqrt{\rho s_{11}^E}$, $\Omega_{11} = (\omega L/2v_{11}^E)$, and $k_{31}^2 = d_{31}^2/\epsilon_0\epsilon_{33}^X s_{11}^E$.

In the resonance discussion, we neglected the damped admittance, because the motional admittance is significantly large due to $\tan(\omega L/2v_{11}^{E*}) \nearrow \infty$. On the contrary, in the antiresonance discussion, we consider basically the subtraction between the damped and motional admittances (due to 180° phase difference); that is, the total admittance should be exactly to zero when the loss is not included, or is only the minimum when we consider the losses (that is, complex parameters) in Eq. (54).

We introduce the normalized admittance $Y' (= Y/j\omega C_0)$ for further calculation:

$$Y' = 1 - k_{31}^2 + k_{31}^2 \frac{\tan(\omega L/2v_{11}^E)}{\omega L/2v_{11}^E} = 1 - k_{31}^2 + k_{31}^2 \frac{\tan(\Omega)}{\Omega}. \quad (65a)$$

Since the expansion series of $\tan \Omega$ is convergent in this case, taking into account Eq. (49) and other loss factors, Eq. (65a,b) leads to

$$\begin{aligned} Y' &= 1 - k_{31}^2 \left[1 - j(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}) \right] \\ &\quad + k_{31}^2 \left[1 - j(2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}) \right] \frac{\tan\Omega^*}{\Omega^*}. \end{aligned} \quad (65b)$$

Note that the "electromechanical coupling k_{31}^2 loss" ($2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}$) contributes significantly in this antiresonance discussion. We separate Y' into conductance G (real part) and susceptance B (imaginary part) as $Y' = G + jB$:

$$G = 1 - k_{31}^2 + k_{31}^2 \frac{\tan\Omega}{\Omega}. \quad (66)$$

$$B = \left(k_{31}^2 - k_{31}^2 \frac{\tan\Omega}{\Omega} \right) (2\tan\theta'_{31} - \tan\delta'_{33} - \tan\phi'_{11}) - \frac{k_{31}^2}{2} \left(\frac{1}{\cos^2\Omega} - \frac{\tan\Omega}{\Omega} \right) \tan\phi'_{11}. \quad (67)$$

The antiresonance frequency Ω_b should satisfy $G = 0$, or $1 - k_{31}^2 + k_{31}^2 \frac{\tan\Omega_b}{\Omega_b} = 0$. Using new parameters,

$$\Omega = \Omega_B + \Delta\Omega_B, \quad (68)$$

$\Delta\Omega_B$ is also a small number, and the first order approximation can be utilized. Neglecting high order term which has two or more small factors (loss factor or $\Delta\Omega_B$), we further approximate Eqs. (66) and (67). Since the antiresonance quality factor Q_B is given by

$$Q_{B,31} = \frac{\Omega_B}{2|\Delta\Omega_B|}, \quad (69)$$

we can now obtain the final formulas for both A-type and B-type mechanical quality factors:

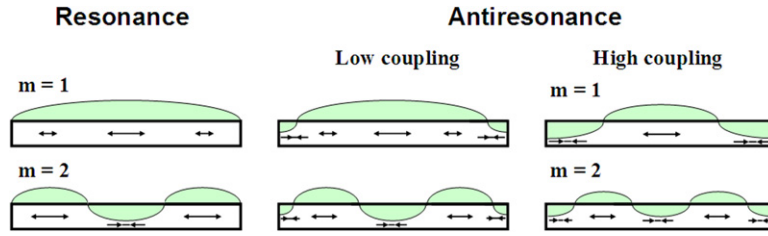


Fig. 11 Strain distribution in the resonant or antiresonant state for a k_{31} type piezoelectric plate.

$$\left\{ \begin{array}{l} \frac{1}{Q_{B,31}} = \frac{1}{Q_{A,31}} - \frac{2}{1 + \left(\frac{1}{k_{31}} - k_{31} \right)^2 \Omega_B^2} (2 \tan \theta'_{31} - \tan \delta'_{33} - \tan \phi'_{11}) \\ 1/Q_{A,31} = \tan \phi'_{11} \end{array} \right. \quad (70)$$

You may understand that k_{31} mode, where the wave propagation direction with the electrode is perpendicular to the spontaneous polarization direction, the primary mechanical resonance (a half wavelength vibration of the plate length) corresponds to the “resonance” mode with the sound velocity s_{11}^E , and the “antiresonance” mode corresponds to the subsidiary mode via the electromechanical coupling. Also from the Eq. (70), we can understand that when $(2 \tan \theta'_{31} - \tan \delta'_{33} - \tan \phi'_{11}) > 0$, $Q_{B,31} > Q_{A,31}$; while $(2 \tan \theta'_{31} - \tan \delta'_{33} - \tan \phi'_{11}) < 0$, $Q_{B,31} < Q_{A,31}$.

Recall the experimental admittance spectrum of the k_{31} rectangular plate ($L = 20$ mm) around its resonance and antiresonance frequencies in Fig. 10. In the Pb-based perovskite piezoelectric ceramics such as PZTs, $Q_{B,31} > Q_{A,31}$ is usually observed; that is, $\tan \theta'_{31} > (\frac{1}{2})(\tan \delta'_{33} + \tan \phi'_{11})$ in PZTs. The intensive “piezoelectric loss” seems to be larger than the “average of dielectric and elastic losses”. Also Eq. (70) indicates how to separately measure the three losses in experiments:

- (1) Obtain $\tan \delta'$ from an impedance analyzer or a capacitance meter at a frequency away (lower) from the resonance/antiresonance range;
- (2) Obtain the following parameters experimentally from an admittance/impedance spectrum around the resonance (A-type) and antiresonance (B-type) range (3 dB bandwidth method): ω_a , ω_b , Q_A , Q_B , and the normalized frequency $\Omega_b = \omega_b L / 2v$;
- (3) Obtain $\tan \phi'$ from the inverse value of Q_A (quality factor at the resonance) in the k_{31} mode;
- (4) Calculate electromechanical coupling factor k_{31} from the ω_a and ω_b with the IEEE Standard equation Eq. (50) or below in the k_{31} mode:

$$\frac{k_{31}^2}{1 - k_{31}^2} = \frac{\pi \omega_b}{2 \omega_a} \tan \left[\frac{\pi(\omega_b - \omega_a)}{2 \omega_a} \right]; \quad (71)$$

- (5) Finally obtain $\tan \theta'$ by Eq. (70) in the k_{31} mode.

Mechanical quality factors Q_A (resonance) and Q_B (antiresonance) for other modes such as k_{33} , k_t , k_p and k_{15} have been calculated and summarized in references Zhuang *et al.* (2010).

Resonance and Antiresonance Vibration Modes

The resonance (A-type) and antiresonance (B-type) states are both mechanical resonance states with amplified strain/displacement states, but they are very different from the electrical driving viewpoints. The mode difference is described by the following intuitive model. In a high electromechanical coupling material with k almost equal to 1, the resonance or antiresonance states appear for $(\tan \omega L / 2v) = \infty$ or 0 [i.e., $\omega L / 2v = (m - 1/2)\pi$ or $m\pi$ (m : integer)], respectively. Based on the fundamental resonance frequency $f_A (= v_{11}^E / 2L)$, the second and third resonance frequencies are represented as $3f_A$ and $5f_A$; the antiresonance frequencies should be $2f_A$, $4f_A$ and $6f_A$, successively. The strain amplitude x_i distribution for each state [calculated using Eq. (43)] is illustrated in Fig. 11. In the resonance state, the strain distribution is basically sinusoidal with the maximum at the center of plate ($x = L/2$) (see the numerator). When ω is close to ω_A , $(\omega_A L / 2v) = \pi/2$, leading to the denominator $\cos(\omega_A L / 2v) \rightarrow 0$. Significant strain amplification is obtained. It is worth noting that the stress X_I is zero at the plate ends ($x = 0$ and L), but the strain x_i is not precisely zero, but is equal to $d_{31} E_z$. According to this large strain amplitudes, large capacitance changes (called “motional capacitance”) are induced, and under a constant applied voltage the current can easily flow into the device (i.e., admittance Y is infinite). To the contrary, at the antiresonance (B-type), the strain induced in the device compensates completely (because extension and compression are compensated in one wave on the specimen length), resulting in no motional capacitance change, and the current cannot flow easily into the sample (i.e., admittance Y zero). Thus, for a high k_{31} material the first antiresonance frequency f_B should be almost twice as large as the first resonance frequency f_A .

It is notable that both resonance and antiresonance states are in the mechanical resonance, which can create large strain in the sample under minimum input electrical energy. When we use a constant voltage supply, the specimen vibration is excited only at the resonance mode, because the electrical power is very small at the antiresonance mode. This provides a common misconception to junior engineers that “the antiresonance is not a mechanical resonance”. In contrast, when we use a constant current supply, the vibration is excited only at the antiresonance, instead. The stress X_I at the plate ends ($x = 0$ and L) is supposed to be zero in both

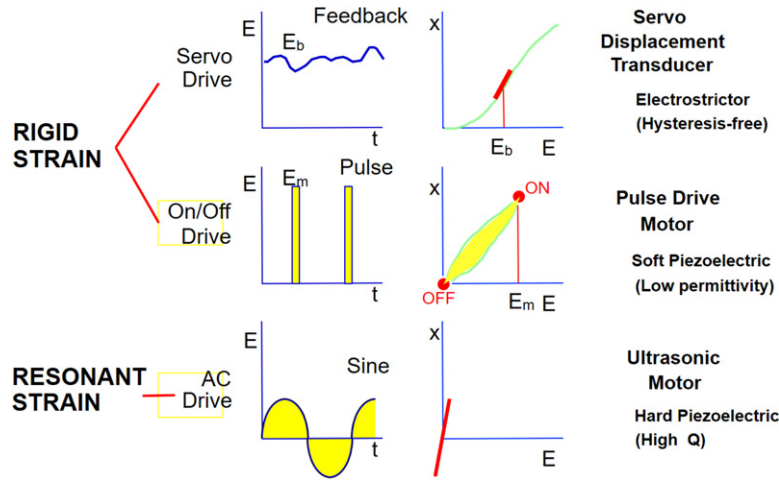


Fig. 12 Classification of piezoelectric/electrostrictive actuators according to the type of drive voltage and the nature of the induced strain.

cases. However, though the strain x_1 at the plate ends is zero/very small (precisely, $d_{31}E_z$, because of low voltage and high current drive) for the resonance, the strain x_1 is large (actually the maximum) for the antiresonance (because of high voltage and low current drive). This means that there is only one vibration node (i.e., zero displacement point) at the plate center for the resonance (Top-left in Fig. 11), and there are additional two nodes at both plate ends for the first antiresonance (Top-right in Fig. 11). The reason is from the antiresonance drive, i.e., high voltage/low current (minimum power) drive due to the high impedance. The converse piezo-effect strain under E directly via d_{31} (uniform strain in the sample) superposes on the mechanical resonance strain distribution (distributed strain with nodes in the sample). Thus, two strains of which have exactly the same level theoretically at the antiresonance for $k_{31} \approx 1$.

In a typical case, where $k_{31} = -0.3$ [sometimes “-” is omitted just to discuss the magnitude], because the damped capacitance $C_d = (1 - k_{31}^2) C_0$ is large, the antiresonance state varies from the previously-mentioned mode and becomes closer to the resonance mode (Top-center in Fig. 11). The low-coupling material exhibits an antiresonance mode where the capacitance change due to the size change (“motional capacitance”) is compensated completely by the current required to charge up the static capacitance (called “damped capacitance”). Thus, the antiresonance frequency f_B will approach the resonance frequency f_A with a similar vibration mode [$f_B = f_A(1 + \frac{4}{\pi^2} k_{31}^2)$] indicates only 3.6% shift from f_A].

It is notable that the mechanical resonance of a k_{31} -type rectangular plate can be excited also under cyclic stress application along the x -axis. In this case, by sweeping the stress frequency, only one mechanical resonance is observed; $f_A (= \nu_{11}^E/2L)$ when the plate specimen is short-circuited, while $f_B = f_A(1 + \frac{4}{\pi^2} k_{31}^2)$ (for a small k_{31} material) when the plate specimen is open-circuited between the top and bottom electrodes. The electrical boundary condition changes significantly the elastic compliance in the piezoelectric materials.

Piezoelectric Materials

Actuator Categories and Materials

Piezoelectric and electrostrictive (or magnetostrictive) actuators are classified into two major categories, based on the type of drive voltage applied to the device and the nature of the strain induced by the voltage as depicted in Fig. 12. They are: (1) rigid displacement devices, for which the strain is induced unidirectionally, aligned with the applied DC field, and (2) resonant displacement devices, for which an alternating strain is excited by an AC field, in particular, at the mechanical resonance frequency (ultrasonic motors). The first category can be further divided into two general types: servo displacement transducers (positioners), which are controlled by a feedback system through a position detection signal, used for optical and precision machinery systems, and pulse drive motors, which are operated in a simple on/off switching mode, suitable for the impact elements of inkjet printers or injection valves.

The material requirements for each class of devices are different, and certain compositions will be better suited for particular applications. The servo displacement transducer suffers most from strain hysteresis and, therefore, a $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ [PMN] electrostrictive material is preferred for this application. It should be noted that even when a feedback system is employed, the presence of a pronounced strain hysteresis general results in a much slower response speed. The pulse drive motor, for which a quick response rather than a small hysteresis is desired, requires a low permittivity material under a current limitation of a power supply. Soft $\text{Pb}(\text{Zr,Ti})\text{O}_3$ [PZT] piezoelectrics are preferred over the high permittivity PMN for this application. The ultrasonic motor, on the other hand, requires a very hard piezoelectric with a high mechanical quality factor, Q_m , in order to maximize the AC strain and to minimize heat generation. Note that the figure of merit for the resonant strain is characterized by $(\frac{8}{\pi^2})dEL \cdot Q_m$ (d : piezoelectric strain coefficient, E : applied electric field, L : sample length, Q_m : mechanical quality factor). Although hard PZT materials have smaller d coefficients, they also have significantly larger Q_m values, thus providing the high resonant strains needed for these devices.

Table 1 Piezoelectric properties of representative piezoelectric materials

Parameter	Quartz	BaTiO ₃	PZT 4	PZT 5H	(Pb,Sm)TiO ₃	NKN-Cu	PVDF-TrFE
d_{33} (pC/N)	2.3	190	289	593	65	99	33
g_{33} (10 ⁻³ Vm/N)57.8	57.8	12.6	26.1	19.7	42	34	380
k_t	0.09	0.38	0.51	0.50	0.50	–	0.30
k_p	–	0.33	0.58	0.65	0.03	0.13	–
$\varepsilon_{33}^{\infty}$	5	1700	1300	3400	175	331	6
Q_m	> 105	–	500	65	900	1052	3–10
T_C (°C)	–	120	328	193	355	340	–

The latter part of this section summarizes the piezoelectric materials: single-crystal materials, piezo-ceramics, piezo-polymers, composites and piezo-films. **Table 1** shows the material parameters of these piezoelectric materials (Ito and Uchino, 1999; Wallace, 1992). Quartz with the highest mechanical quality factor is used for low loss transducers. PZT family shows high d and k suitable for high power transducers. “Soft” PZT such as PZT 5H is for off-resonance actuator applications, while “Hard” PZT is for resonance type ultrasonic motor, transformer and transducer applications. In, particular Sm-doped lead titanates exhibit extremely high mechanical coupling anisotropy (k_t/k_p), suitable for medical transducers. Pb-free (Na,K)NbO₃-based ceramics are focused as the next generation materials, once PZT will be regulated in the future. Piezo-polymer PVDF has small permittivity, leading to high piezo g constant, in addition to mechanical flexibility, suitable to pressure/stress sensor applications.

Single Crystals

Although piezoelectric ceramics are widely used for a large number of applications, single crystal materials retain their utility, being essential for applications such as frequency stabilized oscillators and surface acoustic devices. The most popular single-crystal piezoelectric materials are quartz, lithium niobate (LiNbO₃, LN), and lithium tantalate (LiTaO₃, LT). The single crystals are anisotropic, exhibiting different material properties depending on the cut of the materials and the direction of bulk or surface wave propagation. Quartz is a well-known piezoelectric material. Quartz has a cut with a zero temperature-coefficient. For instance, quartz oscillators, operated in the thickness shear mode of the AT-cut, are used extensively for clock sources in computers with a high mechanical quality factor $Q_M > 10^5$, frequency stabilized ones in TVs and VCRs. On the other hand, an ST-cut quartz substrate with X-propagation has a zero temperature-coefficient for surface acoustic wave, and so is used for SAW devices with high-stabilized frequencies. LN and LT belong to an isomorphous crystal system and are composed of oxygen octahedron. Because these materials have higher electromechanical coupling coefficients for surface acoustic wave than quartz, they occupy important positions in the SAW device application field.

Highly responsive single crystal relaxor ferroelectrics from solid solution systems with a morphotropic phase boundary (MPB) are one of the epochmaking discoveries in piezoelectrics for applications as ultrasonic transducers and electromechanical actuators. Compositions very near the morphotropic phase boundary tend to show the most promise for these applications. Extremely high values for the electromechanical coupling factor ($k_{33} = 92\%–95\%$) and piezoelectric strain coefficient ($d_{33} = 1500$ pC/N) were first reported for single crystals at the MPB of the Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ [PZN-PT] system in 1981 by the author's group (Kuwata *et al.*, 1981; Kuwata and Uchino, 1982). The highest values for the piezoelectric coefficients $d_{33}^* = 1500$ pC/N and electromechanical coupling factors $k_{33}^* = 95\%$ are observed in the morphotropic phase boundary (MPB) composition, 0.91Pb(Zn_{1/3}Nb_{2/3})O₃-0.09PbTiO₃, for the rhombohedral composition only when the single crystal is poled along the perovskite [001] direction, not along [111], which is the direction of the spontaneous polarization. Approximately 10 years after the discovery, Toshiba, Japan (Yanagiwara and Kanai, 1995) and Park *et al.* at the Penn State University (Park and Shrout, 1997) independently reproduced the above findings, and refined data were collected in order to characterize the material for medical acoustic applications. Strains as large as 1.7% can be induced in single crystals from the morphotropic phase boundary (MPB) composition 0.92PZN-0.08PT of this system in the [001] orientation.

The mechanism for the enhanced electromechanical coupling is basically from the large shear coupling through d_{15} , which is generally dominant for perovskite piezoelectrics. The applied electric field should therefore be applied such that its direction is somewhat ($\sim 50^\circ$) canted from the spontaneous polarization direction in order to produce the optimum piezoelectric response. The exceptionally high strain generated in materials with compositions near the morphotropic phase boundary (up to 1.7%) is associated additionally with the field-induced phase transition from the rhombohedral to the tetragonal phase. Recent studies are shifting to single crystals at the MPB of the Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ [PMN-PT] system, which is isomorphic with PZN. Because of the significant cant angle between the spontaneous polarization and electric field directions, complicated multi-domain structures are created in a single crystal inevitably. Accordingly, so-called “domain engineering” concept came up to further explain the electromechanical coupling enhancement via the domain-domain interaction and domain interface/wall (Wada, 2015).

Polycrystalline Materials

Barium titanate BaTiO₃ (BT) is one of the most thoroughly studied and most widely used capacitor materials with a perovskite type crystal structure, after the discovery independently in Japan, US, Russia, and Germany during World War II. Just below the Curie temperature (120°C), the vector of the spontaneous polarization points in the [001] direction (tetragonal phase), below 5°C

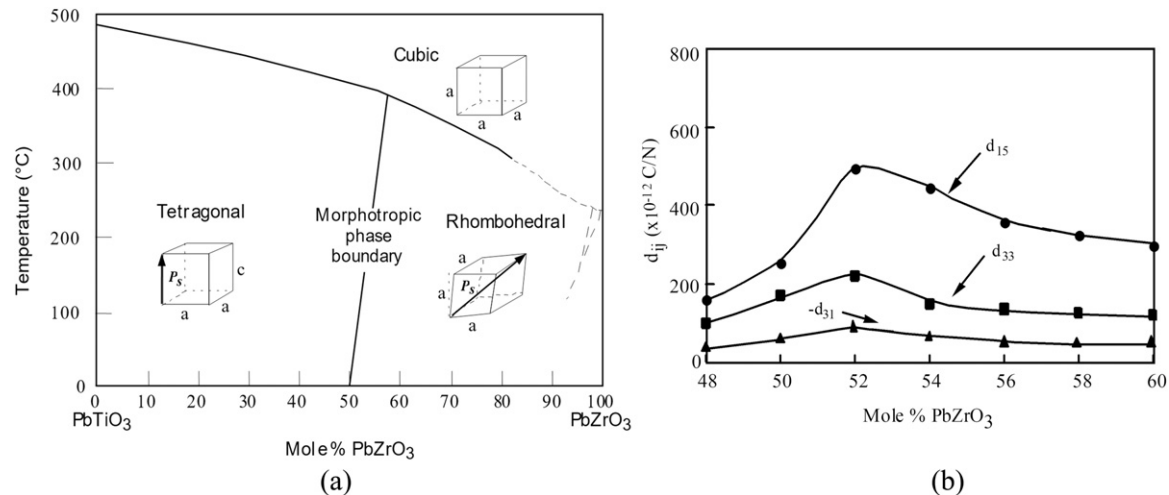


Fig. 13 (a) Phase diagram of lead zirconate titanate (PZT). (b) Dependence of several d constants on composition near the morphotropic phase boundary in the PZT system.

it reorients in the [011] (orthrhombohedral phase) and below -90°C in the [111] direction (rhombohedral phase), successively. Though the initial application was for Langevin-type piezoelectric vibrators, after the discovery of PZT's, the applications to piezoelectric devices faded out until recently when Pb-free materials have been focused.

Lead zirconate titanate (PZT) solid solution systems were discovered in 1954 by Japanese researchers, (Sawaguchi *et al.*, 1951) through systematic studies on BT-isomorphic perovskite materials. Fig. 13(a) shows the phase diagram of lead zirconate titanate (PZT), where the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral phases exists around 52 PZ - 48 PT compositions. However, the enormous piezoelectric properties were discovered by Jaffe (1955), Clevite Corporation, and Clevite took the most important PZT patent for transducer applications. Because of this strong basic patent, Japanese ceramic companies were encouraged actually to develop ternary systems to overcome the performance, and more importantly, to escape from the Clevite's patent; that is, PZT + a complex perovskite such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Panasonic), $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Toshiba), $\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (NEC), $\text{Pb}(\text{Sb}_{1/2}\text{Sn}_{1/2})\text{O}_3$, $\text{Pb}(\text{Co}_{1/2}\text{W}_{1/2})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (Du Pont), which are the basic compositions in recent years.

The crystalline symmetry of this solid-solution system is determined by the Zr content as shown in Fig. 13(a) (another low temperature Rhombohedral phase is omitted in this figure). Pure lead titanate (PT) has a tetragonal ferroelectric phase of the perovskite structure. With increasing Zr content, x , the tetragonal distortion decreases and at $x > 0.52$ the structure changes from the tetragonal $4mm$ phase to another ferroelectric phase of rhombohedral $3m$ symmetry. The line dividing these two phases is called the morphotropic phase boundary (MPB). The boundary composition is considered to have both tetragonal and rhombohedral phases coexisting together, or exhibits the phase transition between each other under electric field. Fig. 13(b) shows the dependence of several piezoelectric d constants on composition near the MPB. The d constants have their highest values near the MPB. This enhancement in piezoelectric effect is attributed to the increased ease of reorientation of the polarization under an applied electric field.

Doping the PZT material with "donor" or "acceptor" ions changes its properties dramatically. Donor doping with ions such as Nb^{5+} or Ta^{5+} provides "soft" PZTs, like PZT-5, because of the facility of domain motion due to the resulting Pb-vacancies. On the other hand, acceptor doping with Fe^{3+} or Sc^{3+} leads to "hard" PZTs, such as PZT-8, because the oxygen vacancies will pin the domain wall motion.

The end member of PZT, lead titanate has a large crystal distortion. PbTiO_3 has a tetragonal structure at room temperature with its tetragonality $c/a = 1.063$. The Curie temperature is 490°C . Densely sintered PbTiO_3 ceramics cannot be obtained easily, because they break up into a powder when cooled through the Curie temperature due to the large spontaneous strain. Lead titanate ceramics modified by adding a small amount of additives exhibit a high piezoelectric anisotropy. Either $(\text{Pb},\text{Sm})\text{TiO}_3$ (Takeuchi *et al.*, 1982) or $(\text{Pb},\text{Ca})\text{TiO}_3$ (Yamashita *et al.*, 1981) exhibits an extremely low planar coupling, that is, a large k_t/k_p ratio. Here, k_t and k_p are thickness-extensional and planar electro-mechanical coupling factors, respectively. Since these transducers can generate purely longitudinal waves through k_t associated with no transverse waves through k_{31} , clear ultrasonic imaging is expected without "ghost" caused by the transverse wave. $(\text{Pb},\text{Nd})(\text{Ti},\text{Mn},\text{In})\text{O}_3$ ceramics with a zero temperature coefficient of surface acoustic wave delay have been developed as superior substrate materials for SAW device applications (Ito *et al.*, 1979).

Relaxor Ferroelectrics

Relaxor ferroelectrics can be prepared either in polycrystalline form or as single crystals. Different from the previously mentioned normal ferroelectrics such as BT and PZT's, they exhibit a broad phase transition from the paraelectric to ferroelectric state, a strong

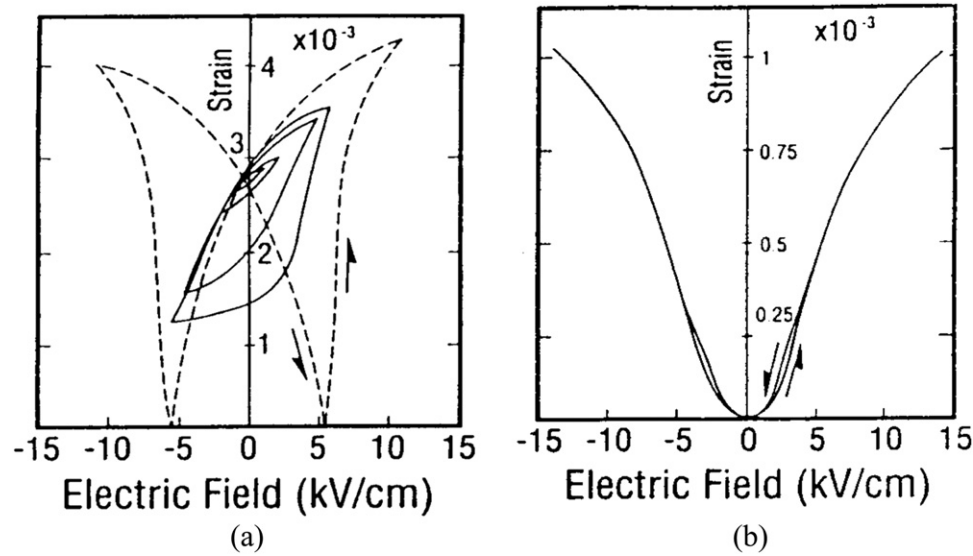


Fig. 14 Typical strain curves for a piezoelectric lead zirconate titanate (PZT) based (a) and an electrostrictive lead magnesium niobate (PMN) based ceramic (b).

frequency dependence of the giant dielectric constant (i.e., dielectric relaxation) and a weak remnant polarization. Lead-based relaxor materials have complex disordered perovskite structures.

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) ceramics are highly suitable for actuator applications, which are easily poled when the poling field is applied near the transition temperature, but they are depoled completely when the field is removed as the macrodomain structure reverts to microdomains (with sizes on the order of several 100 Å). This microdomain structure is believed to be the source of the exceptionally large electrostriction exhibited in these materials. The usefulness of the material is thus further enhanced when the transition temperature is adjusted to near room temperature. The longitudinal induced strain at room temperature as a function of applied electric field for 0.9PMN-0.1PbTiO₃ ceramic is shown in Fig. 14(b) (Uchino *et al.*, 1981; Uchino, 1986). Notice that the order of magnitude of the electrostrictive strain (10^{-3}) is similar to that induced under unipolar drive in PLZT (7/62/38) through the piezoelectric effect (Fig. 14(a)). An attractive feature of this material is the near absence of hysteresis, while the non-linear strain behavior ($\epsilon = ME^2$) requires a sophisticated drive circuit.

This relaxor ferroelectric 0.9PMN-0.1PT also exhibits an induced piezoelectric effect under DC bias electric field. That is, the electromechanical coupling factor k_t varies with the applied DC bias field. As the DC bias field increases, the coupling increases and saturates. Since this behavior is reproducible, these materials can be applied as ultrasonic transducers which are tunable by the bias field (Takeuchi *et al.*, 1990).

The superior performances in single-crystal relaxor ferroelectrics with the morphotropic phase boundary (MPB) composition have already been discussed in Section “Single Crystals”.

PVDF

Thank to Kawai's efforts, polyvinylidene difluoride (PVDF or PVF₂) was discovered in 1969 (Kawai, 1969). Though the piezoelectric d constant is not as high as piezo-ceramics, high piezoelectric g constant due to small permittivity is attractive from the sensor application viewpoint.

The PVDF is a polymer with monomers of CH₂CF₂. Since H and F have positive and negative ionization tendency, the monomer itself has a dipole moment (though covalent bonding). Crystallization from the melt forms the non-polar α -phase, which can be converted into the polar β -phase by a uniaxial or biaxial drawing operation; the resulting dipoles are then reoriented through electric poling (see Fig. 15). Large sheets can be manufactured and thermally formed into complex shapes. The copolymerization of vinylidene difluoride with trifluoroethylene (TrFE) results in a random copolymer (PVDF-TrFE) with a stable, polar β -phase. This polymer need not be stretched; it can be electrically-poled directly as formed. A thickness-mode coupling coefficient k_t of 0.30 has been reported. Piezoelectric polymers have the following characteristics: (a) small piezoelectric d constants (for actuators) and large g constants (for sensors), due to small permittivity, (b) light weight and soft elasticity, leading to good acoustic impedance matching with water or the human body, (c) a low mechanical quality factor Q_M , allowing for a broad resonance band width, though the heat generation is problematic during continuous operation. Such piezoelectric polymers are used for directional microphones and ultrasonic hydrophones.

Zhang *et al.* reported that the field induced strain level can be significantly enhanced up to 5% by using a high-energy electron irradiation onto the PVDF films, leading to an electrostrictive performance (Bharti *et al.*, 2000).

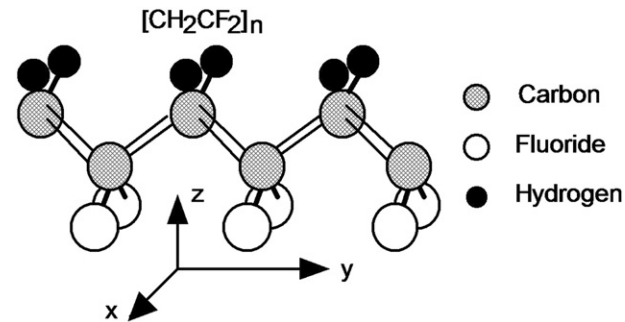


Fig. 15 Molecular structure of polyvinylidene difluoride (PVDF).

Pb-Free Piezo-Materials

In 2006, European Union started RoHS (Restrictions on the use of certain Hazardous Substances), which explicitly limits the usage of lead (Pb) in electronic equipment. Basically, we may need to regulate the usage of lead zirconate titanate (PZT), current most famous piezoelectric ceramics, in the future. Japanese and European societies may experience the governmental regulation on the PZT usage in these 10 years. Pb (lead)-free piezoceramics have started to be developed after 1999. The Pb-free materials include (1) (K,Na)(Ta,Nb)O₃ based, (2) (Bi,Na)TiO₃, and (3) BaTiO₃, which reminds us “the history will repeat” (i.e., “piezoelectric Renaissance”) (Uchino, 2019).

Above non-toxicity and disposability, Murata Manufacturing Co. is further seeking bio-degradable devices with using L-type poly-lactic acid (PLLA). PLLA is made of vegetable corn-based composition (Anon3). Because it exhibits pure piezoelectric without pyroelectric effect, the stress sensitivity is sufficient for leaf-grip remote controllers for Nintendo computer game usages, which do not need a very long lifetime.

Composites

Piezo-composites comprised of a piezoelectric ceramic and a polymer phase are promising materials because of their excellent and readily tailored properties. The geometry for two-phase composites can be classified according to the dimensional connectivity of each phase into 10 structures; 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3 and 3-3 (Newnham, 1978). A 1-3 piezocomposite, such as the PZT-rod/polymer composite is the most promising candidate. The advantages of this composite are high thickness coupling factors, low acoustic impedance, good acoustic impedance matching to water or human tissue, mechanical flexibility, broad bandwidth in combination with a low mechanical quality factor and the possibility of making undiced arrays by structuring the electrodes. The thickness-mode electromechanical coupling of the composite can exceed the k_t (0.40–0.50) of the constituent ceramic, approaching almost the value of the rod-mode electromechanical coupling, k_{33} (0.70–0.80) of that ceramic (Smith, 1989). Piezoelectric composite materials are especially useful for underwater sonar and medical diagnostic ultrasonic transducer applications.

Piezoelectric Actuator Designs

Actuator Design Classification

A classification of piezoelectric actuators based on structure type is presented in Fig. 16, among which the multilayer (ML) and unimorph/bimorph types are the most commonly used structures. Although the multilayer type produces only relatively modest displacements (10 μ m), it offers a respectable generative force (1 kN), a quick response speed (10 μ sec), long lifetime (10¹¹ cycles), and a high electro-mechanical coupling factor k_{33} (70%). In contrast, the unimorph/bimorph type provides large displacements (300 μ m), but can only offer a relatively low generative force (1 N), a much slower response speed (1 msec), a shorter lifetime (10⁸ cycles) and a rather low electromechanical coupling factor k_{eff} (10%). Cymbal/Moonie designs composed of a piezo-ceramic layer sandwiched by two metal endcaps (cymbal or concaved shape) exhibit intermediate performances, 100 μ m displacement, 100 N and 100 μ sec response, which are actually most desired specifications by the users. Recently because of the portable equipment requirement for a low driving voltage (less than 15 V with a battery), most of the designs use an ML piezo-component as a base, such as multimorphs and ML cymbals/moonies.

Two preparation processes are possible for multilayer ceramic devices: “cut-and-bond method” and “tape-casting method” (invented by Uchino *et al.*, 1980). Though the tape-casting method requires expensive fabrication facilities and sophisticated techniques, it is suitable for the mass-production of million pieces per month, which accelerated the ML actuator applications for consumer products.

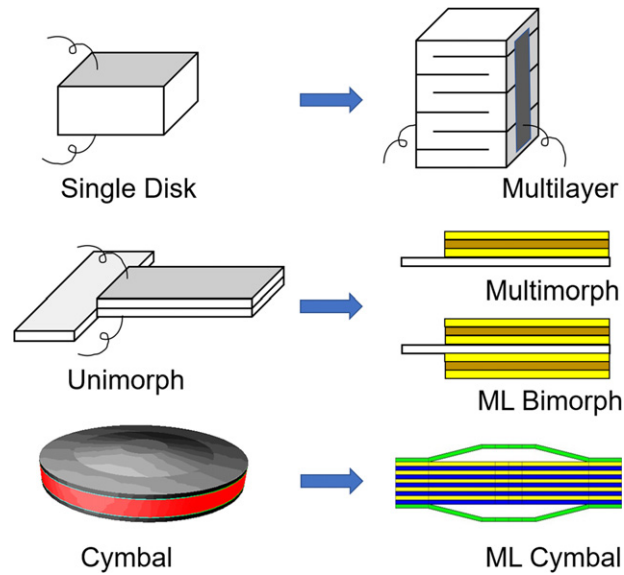


Fig. 16 Piezoelectric actuator designs: multilayer, bimorph, and cymbal/moonie structures.

Thin/Thick-Films

Though the thin-film configuration is sometimes categorized as a part of composites, due to specific constraints such as thickness of films, stress from the substrate, and epitaxial growth/film crystal orientation, special attentions are required, so that we discuss the film structure as a device design.

Both zinc oxide (ZnO) and aluminum nitride (AlN) are simple binary compounds with a Wurtzite-type structure, which can be sputter-deposited as a c-axis oriented thin film on a variety of substrates. ZnO has large piezoelectric coupling and thin films of this material are widely used in bulk acoustic and surface acoustic wave devices. The fabrication of highly oriented (along c) ZnO films have been studied and developed extensively. However, the performance of ZnO devices is limited, due to their low piezoelectric coupling (20%–30%).

“Micro Electro-Mechanical System” (MEMS) is now popular using the so-called “micro-machining process” used conventionally to fabricate silicon devices. One of the first practical MEMS device, PZT micropump, for blood tester created in the end of 1990s is illustrated in Fig. 17 (Kalpat *et al.*, 2001). The blood sample and test chemicals entering the system through the two inlets, identified in Fig. 17, are mixed in the central cavity, and finally are passed through the outlet for analytical instrument. The movement of the liquids through the system occurs through the bulk bending of the PZT diaphragm in response to the drive potential provided by the “interdigital surface electrodes”. The key issue for the actuator-type MEMS device is the output mechanical power level, which should be > 1 mW for soaking blood from a human body. Since the PZT handling power is limited around 30 mW/mm^3 (higher power generates significant heat), thick films thicker than $30 \mu\text{m}$ are usually desired from the electro-mechanical actuator application viewpoint. Thin films less than $1 \mu\text{m}$ have been commercialized for sensor developments or zero-load optical reflector/mirror control applications, but are useless for practical actuator applications.

Drive/Control Technologies

Drive Methods of Piezoelectric Actuators

Piezoelectric actuators are classified into two major categories, based on the type of drive voltage applied to the device and the nature of the strain induced by the voltage as shown in Fig. 12. They are: (1) rigid displacement devices, for which the strain is induced unidirectionally, aligned with the applied DC field, and (2) resonant displacement devices, for which an alternating strain is excited by an AC field at the mechanical resonance frequency (ultrasonic motors). The first category can be further divided into two general types: servo displacement transducers (positioners), which are controlled by a feedback system through a position detection signal, and pulse drive motors, which are operated in a simple on/off switching mode. The response of the resonant displacement devices is not directly proportional to the applied voltage, but is dependent on the drive frequency.

Refer to the admittance spectrum (Fig. 10) of a k_{31} type piezoelectric (PZT) plate specimen with the resonance frequency around 86 kHz. When the operating frequency is lower than 10 kHz, this is considered as “off-resonance” (or pseudo-DC) drive, and its characteristic is purely “capacitive” with the admittance ($j\omega C$) phase lag of 90° . When the operating frequency is 86 kHz or 89 kHz, the characteristic become “resistive” with the phase lag of 0° , which corresponds to the resonance or antiresonance frequency. In order to induce the same level of vibration velocity, low voltage & high current or high voltage & low current is required at the resonance or antiresonance drive, respectively. As already introduced in Section “Admittance Around Resonance

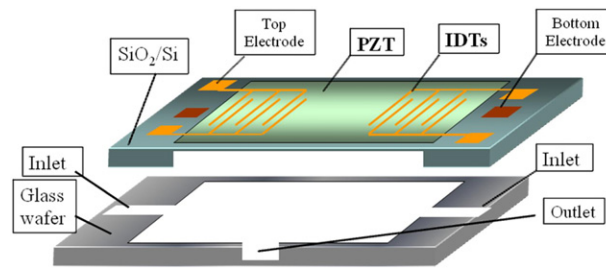


Fig. 17 A schematic diagram of the structure of a PZT micropump. Actual size: 4.5 mm × 4.5 mm × 2 mm.

and Antiresonance”, due to the higher Q_m , the antiresonance frequency drive exhibits higher efficiency (i.e., heat generation suppression!) than the resonance drive (Hirose *et al.*, 1996b). The author’s group also demonstrated an operating frequency at 88 kHz in the inductive ($1/j\omega L$) region in order to minimize the required input drive power for obtaining the same mechanical vibration level (Yuan *et al.*, 2017). To the contrary, the pulse drive includes wide-range of frequencies (pseudo-DC to multiple higher-order resonance frequencies), which exhibit linear or parabolic total displacement, in addition to the overshoot and/or vibration ringing, depending on the pulse voltage shape applied.

Pseudo-DC Drive – Negative Capacitance Usage

Most of the conventional linear and switching power systems have been developed for driving primarily resistive loads such as electromagnetic motors. For example, when a switching power system in driving a resistive load, 90% of the input 160 W can be spent in the resistive load (90% efficiency), while only 2% can be used in a capacitive load (2% efficiency). 90% of the input power is spent out in the power supply (mostly as heat) in the capacitance drive. We had better consider much better driving scheme for solid-state capacitive components such as multilayer piezo-actuators under off-resonance drive. When dealing with capacitive components, it is important to consider energy flow (“real power” $V \cdot I \cos \phi$) rather than “apparent power” flow ($V \cdot I$). The key to escape from this electric impedance mismatching is to insert a reactive (or inductive) component in the driving system in series to the capacitive device. Knowing that the conventional coil inductor kills the size and weight (and Joule loss) in the power supply significantly, Knowles *et al.* at Qortek, PA introduced a “negative capacitance” in the switching power system (Anon). The negative capacitance $-C_d/T$, where C_d is the “damped capacitance” of the piezoelectric device, is inserted in series with the R-C circuit. Though the usage of power is still 2% (in case of small electromechanical coupling factor k such as 20%), the remaining 98% will be recovered without losing much as heat in the power system because of the negative capacitance, leading to a high efficiency 98%. Note that since the actually consumed electric energy level is just 4–10 W, depending on the mechanically consumed energy in the piezo-actuator (in addition to the energy loss in the power circuit), the total size/weight of the power system is significantly smaller than the conventional ones.

Inductive Region Drive – Positive Capacitance Usage

Shi *et al.* (2014). indicated that the mechanical quality factor Q_m exhibits the maximum at a frequency in-between the resonance and antiresonance frequencies, because of a particular combination of three losses; piezoelectric and dielectric and elastic factors. Accordingly, Yuan *et al.* (2017). practically demonstrated on a Langevin underwater transducer that the required input drive power become minimum at the particular frequency in the inductive ($1/j\omega L$) region by coupling a capacitor with Class E Inverter for obtaining the same mechanical vibration level (Yuan *et al.*, 2017).

Pulse Drive Technique

Different from an Equivalent Circuit analysis, when we use a “continuum piezoelectric media” analysis, the displacement response to a “pulse drive” exhibits a linear straight strain/displacement response, rather than a sinusoidal or harmonic response. Experimental results for a piezoelectric bimorph exhibited that the ringing tip displacement shows a triangular shape (not a sinusoidal) under a pulse/step drive, as shown in Fig. 18(a) (Sugiyama and Uchino, 1986). Note also that when the pulse width or step rise time is adjusted exactly to its resonance period, the ringing can completely be shut off. In other words, the piezo-system can act as a ‘damper’ with tuning the driving voltage shape without losing any energy, different from a case of an elastic damper. Fig. 18(b) shows the bimorph tip displacement response to a pseudo-step voltage, which indicates the ideal no-overshoot, no-ringing response, when the rise time is adjusted exactly to its resonance period.

This suggests an empirical process on how to suppress the overshoot and/or ringing in a piezoelectric actuator system: (1) By applying a relatively steep rising voltage to the actuator, we can obtain the system resonance period from the time period between the overshoot peak and the successive peak point. (2) By adjusting the voltage rise time exactly to the resonance period next time, we can eliminate the overshoot and/or ringing of the vibration. In other words, without using a mechanical damper (which loses energy), we can diminish vibration overshoot or ringing just by adjusting the pulse width or rise time of the applied voltage, which

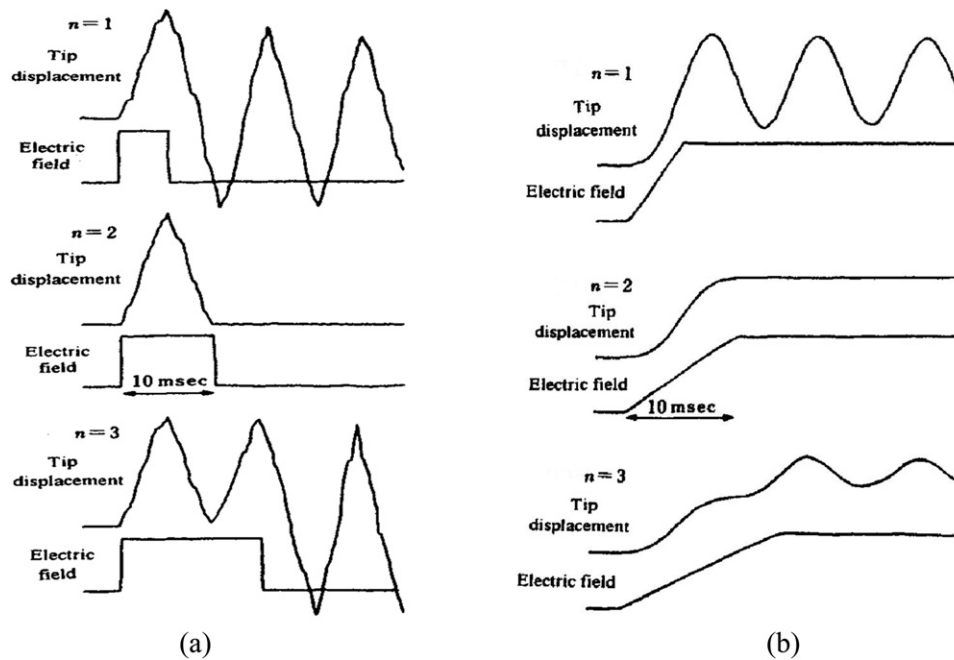


Fig. 18 Measurement on a bimorph tip displacement generated by a pulse voltage (a), and a pseudo step voltage (b).

does not lose energy in fact. This procedure can be adopted to the cutting edge/tool position change with a piezoelectric actuator in lathe, milling or other cutting machines.

Actuator Applications of Piezoelectrics

When piezoelectric materials are used as actuators, the T_C of which should be much above the room temperature (or, using temperature) because heat generation is rather large under high-power drive. Piezoelectric ML precision positioners have already been installed in precision lathe machines, semiconductor manufacturing apparatuses and office equipment. In this section, best-selling products, diesel injection valve system (pulse drive) and camera module (ultrasonic motor) are introduced, followed by 2-degree of freedom impact motor for medical catheter applications.

Piezoelectric Multilayer Actuators for Automobile

Diesel engines are recommended rather than regular gasoline cars from the energy conservation and global warming viewpoint. When we consider the total energy of gasoline production, both well-to-tank and tank-to-wheel, the energy efficiency, measured by the total energy required to realize unit drive distance for a vehicle (MJ/km), is of course better for high octane gasoline than diesel oil. However, since the electric energy required for purification is significant, the gasoline is inferior to diesel fuel (Anon2). As well known, the conventional diesel engine, however, generates toxic exhaust gases such as SO_x and NO_x due to insufficient burning of the fuel. In order to solve this problem, new diesel injection valves were developed by Siemens, Bosch and Toyota with piezoelectric multilayered (ML) actuators. Fig. 19(a) shows such a common-rail type diesel injection valve with a ML piezo-actuator which produces high pressure fuel and quick injection control. Owing to the large force and quick response of the PZT ML actuator, we could realize very fine mist of diesel fuel in order to be burned effectively. See the diesel fuel injection timing chart in Fig. 19(b) with 5–7 injections per engine cycle, which requires 100 μ sec responsibility. The highest reliability of these devices at an elevated temperature (150°C) for a long period (10 years) has been achieved (Fujii, 2005). The piezoelectric actuator is namely the key to increase burning efficiency and minimize the toxic exhaust gases. Current research target includes (a) the Cu internal electrode usage for replacing the Ag-Pd electrode to reduce the manufacturing cost of the piezo-ML's, and (b) Pb-free piezo-ceramics for replacing the PZT to overcome the RoHS regulation.

Ultrasonic Motors (USM) for Camera Modules

A micro motor called "metal tube type" consisting of a metal hollow cylinder and two PZT rectangular plates was developed by The Penn State University in the late 1990s [see Fig. 20(a)] (Koc et al., 2002). When one of the PZT plates is driven (single phase drive), Plate X, a bending vibration is excited basically along x axis. However, because of an asymmetrical mass (Plate Y), another hybridized bending mode is excited with some phase lag along y axis, leading to an elliptical locus in a clockwise direction, like a

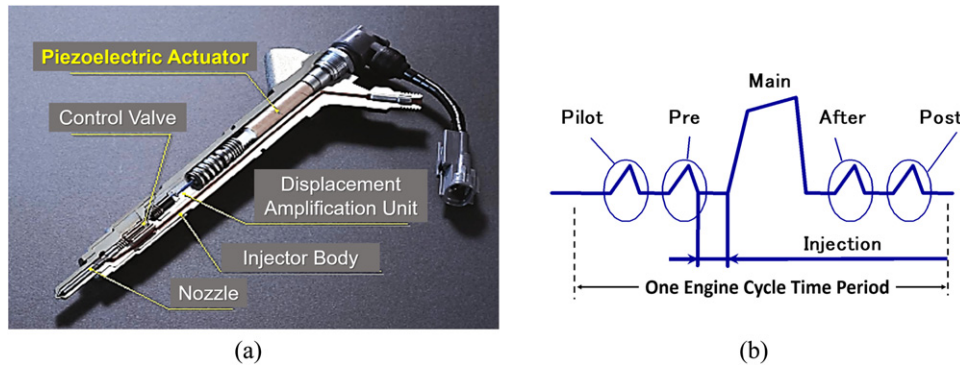


Fig. 19 (a) Common rail type diesel injection valve with a piezoelectric multilayer actuator [Courtesy by Denso Corporation]. (b) Diesel fuel injection timing chart.

'Hula-Hoop' motion. The rotor of this motor is a cylindrical rod with a pair of stainless ferrules pressing down with a spring. The metal cylinder motor 2.4 mm in diameter and 12 mm in length was driven at 62.1 kHz in both rotation directions. No-load speed of 1800 rpm and output torque of up to 1.8 mN•m were obtained for rotation in both directions under an applied rms voltage of 80 V. A rather high maximum efficiency of about 28% for this small motor is a noteworthy feature (Koc *et al.*, 2002; Cagatay *et al.*, 2003). Various modifications were made for the stator, including a type with four PZT plates, arranged symmetrically and driven by two-phase (sine and cosine) voltages.

In collaboration with The Penn State University, Samsung Electromechanics, Korea developed the world-first zoom and focus mechanism for mobile phones with two micro rotary motors in 2003. Two micro metal tube motors with 2.4 mm diameter and 14 mm length were installed to control zooming and focusing lenses independently in conjunction with screw mechanisms, as illustrated in Fig. 20(b) (Uchino, 2004). A screw is rotated through a pulley, which is then transferred to the lens up-down motion. The square chip (3×3 mm²) on the camera module in Fig. 20(c) is a high-frequency drive voltage supply. Newscale Technologies (Victor, NY) integrated a screw in the metal tube motor, and commercialized "squiggle motors" worldwide for camera module applications, with a partnership with ALPS, Tamron, and TDK-EPC (Anon1). Samsung Electromechanics is now utilizing much smaller micro ML chip linear USM's for the Galaxy series camera modules due to the thinner design necessity (Koc *et al.*, 2006).

2DOF Inertial Motors

Conventional inertial motors

In order to simplify the motor structure and make the manufacturing cost inexpensive in comparison with ultrasonic motors, an inertial motor have been investigated. The inertial motor was firstly commercialized by Konica-Minolta, Japan, called as Smooth Impact Drive Mechanism (SIDM) using an ML piezo-element (Okamoto *et al.*, 2004). The principle of the "stick & slick" motion on a drive rod is illustrated in Fig. 21(a). By applying a sawtooth shaped voltage on a piezoelectric actuator, alternating slow expansion and quick shrinkage are excited on a drive friction rod (see Fig. 21(b)). A slider placed on the drive rod will "stick" on the rod due to friction during a slow expansion period, while it will "slick/slide" during a quick shrinkage period, so that the slider moves from the left to the right. When the voltage saw shape is reversed opposite motion can be obtained.

When we increase the drive frequency of the SIDM up to its mechanical resonance, aiming at the improvement in speed and thrust, we found a problem in its drive voltage form: the saw-type voltage wave cannot generate the saw-type displacement with approaching the resonance frequency (i.e., the displacement becomes sinusoidal!), as shown in Fig. 21(b) (Tuncdemir *et al.*, 2011).

Asymmetric rectangular pulse drive technique

- Higher-order harmonics combination

In order to produce the "stick & slick" motion of the moving body, the "saw-tooth moving-rod" vibration is essential. Taking into account that the "saw" wave can be expressed by a Fourier transform as

$$\begin{aligned}
 f(x) &= \frac{a_0}{2} + \sum_{n=1}^{\infty} [a_n \cos(nx) + b_n \sin(nx)] \\
 &= 2 \sum_{n=1}^{\infty} \left[\frac{(-1)^{n+1}}{n} \sin(nx) \right] \quad [for \ x - \pi \neq 2\pi Z]
 \end{aligned} \tag{72}$$

Morita's group proposed the 1st and 3rd harmonic combination drive for exhibiting a saw-type displacement mode (Nishimura and Morita, 2010). However, this harmonic combination drive requires multiple voltage sources according to the number of higher-order harmonics to be considered.

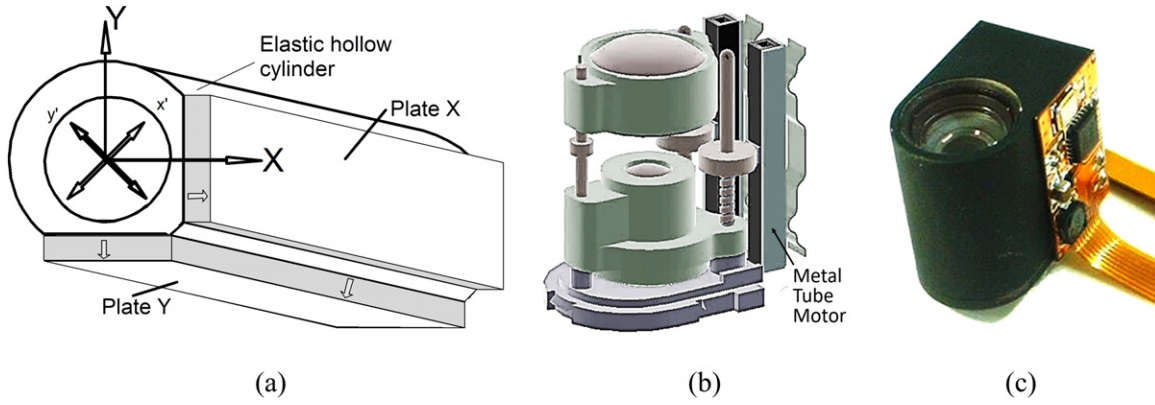


Fig. 20 (a) Structure of a “Metal tube” USM motor using a metal tube and two rectangular PZT plates. (b) Structure of the camera auto zooming/focusing mechanism with two metal tube USM’s. (c) Photo of the camera module in a Samsung cellular phone.

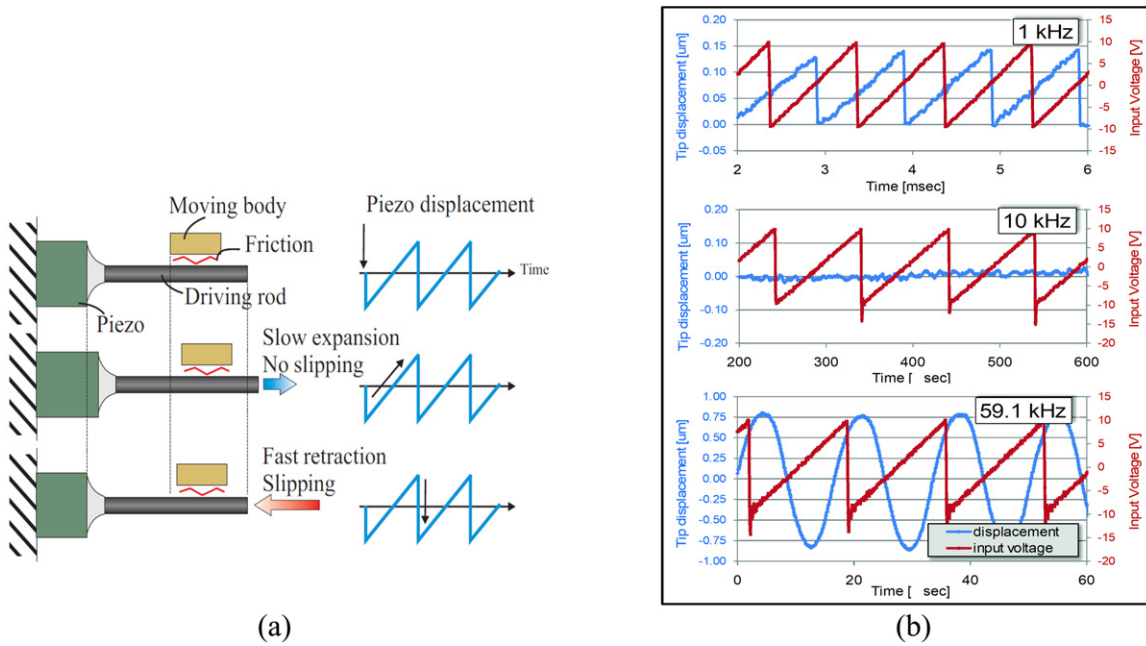


Fig. 21 (a) Principle of the “stick & slick” motion of the slider on a drive rod. (b) Frequency dependence of the output displacement on saw-type input voltage. Reproduced from (a) Okamoto, Y., Yoshida, R., Sueyoshi, H., 2004. Konica Minolta Tech. Report 1, 23. (b) Tuncdemir, S., Ural, S.O., Koc, B., Uchino, K., 2011. Design of translation rotary ultrasonic motor with slanted piezoelectric ceramics. Jpn. J. Appl. Phys., 50 (2011), 027301.

- Variable duty-ratio square pulse drive

In order to simplify the drive circuit and reduce the system cost, Tuncdemir *et al.* proposed to use a rectangular voltage wave at the resonance frequency with variable duty ratio, as schematically illustrated in Fig. 22(a) (Tuncdemir *et al.*, 2011; Uchino *et al.*, 2011). Because an asymmetric square waveform can be written as Fourier functions:

$$V(t, D) = \sum_{n=1}^{\infty} [a_n \cos(n\omega t) + b_n \sin(n\omega t)] \quad (73)$$

where $a_n = \frac{2A}{n\pi} \sin(2n\pi D)$ and $b_n = \frac{2A}{n\pi} [1 - \cos(2n\pi D)]$, we can apply 1st, 2nd, 3rd harmonic voltage without using different power supplies.

2DOF miniature USM with impact drive

Tuncdemir *et al.* developed a “Translational-Rotary” multi Degree-of-Freedom (DoF) piezoelectric ultrasonic motor as pictured in Fig. 22(b), aiming at a tweezer application with medical catheters. The stator of this motor consists of four slanted piezoelectric

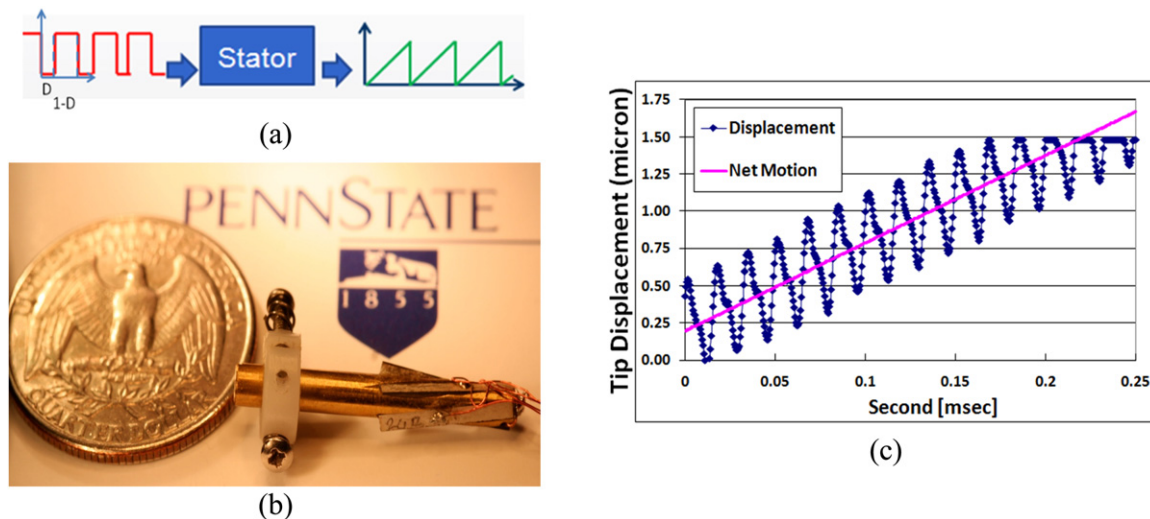


Fig. 22 (a) Schematic illustration of the Asymmetric rectangular voltage drive principle for generating a sawtooth displacement. (b) Translational-rotary ultrasonic motor with four slanted PZT ceramic plates. (c) Practical slider motion of the “translational-rotary” inertial motor under a drive condition of 59 kHz and $D = 67\%$.

plates bonded on a metal rod. Dual function output, which is observed on the ring-shaped slider, is controlled by single source excitation signal. The PZT ceramics are excited at the resonance frequency of first longitudinal mode (~ 59 kHz) for translational operation, or of first torsional mode (~ 34 kHz) for rotational output motion. The ATILA computer simulation of the tip displacement and the measured tip displacement for various duty ratio of the rectangular wave voltage exhibited semi-sawtooth motion of the stator rod. The slider monitoring determined the drive condition (frequency and duty ratio) for obtaining translational or rotary operation on the slanted-PZT-plate inertial motor. Practical slider “translational motion” under a drive condition of 59 kHz and $D = 67\%$ is demonstrated in Fig. 22(c). Note smooth linear shift of the average position, superposed with zig-zag vibrational displacement, which is significantly different from the normal ultrasonic motor slider shift.

Conclusion

Because the “piezoelectricity” exhibits rather unique “compact actuator” performance without finding strong competitors (electromagnetic counterpart motors/transformers are very inferior in terms of efficiency in compact component domains smaller than 30 W), actuator applications are expanding significantly in these days.

Though relatively large investments and research efforts are being put on piezoelectric MEMS/NEMS and “nano energy harvesting” devices, a positive comment is not provided at the moment, except for the sensor applications. Even for medical applications, obtained/reported energy level $\text{pW} \sim \text{nW}$ from one component (this level is called “sensor”, not “actuator” nor “energy harvester”, in practice) is a useless level, which is originated from inevitable small volume of the used piezoelectric material (i.e., thin films). The reader needs to understand that minimum 1 mm^3 PZT is required for generating a couple of mW (minimum level for practical actuator and energy harvesting applications). The researches with thick films (thicker than $30 \mu\text{m}$) are highly encouraged. Refer to a review paper (Akedo *et al.*, 2017) on the “aerosol deposition (AD)” technique by Akedo, Ryu *et al.*

Finally the author points out five key trends for providing the future perspectives of piezoelectric devices; “Performance to Reliability” (Pb-free piezoelectrics, bio-degradable piezo-polymer, low loss piezoelectric), “Hard to Soft” (foldable piezo-polymer film, PMN/PZN single crystals), “Macro to Nano” (piezo-MEMS), “Homo to Hetero” (flexoelectricity, monomorph) and “Single to Multi-functional” (magnetoelectrics, photostriction). In the application area, the global regime for “ecological sustainability” particularly accelerated new developments in ultrasonic disposal technology of hazardous materials, diesel injection valves for air pollution, and piezoelectric renewable energy harvesting systems. Refer to Uchino (2014, 2017) for further information.

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Flexible and Wearable Strain/Pressure Sensors

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Abstract

Flexible sensors, a critical device in the field of flexible and wearable electronics, have attained a lot of interest due to their diverse applications in various fields. Over the years, many researchers worldwide have utilized different synthesis methods, emerging functional material systems, and their composites/hybrids for flexible physical sensors and found that a simple preparation method to enhance the device's performance is still a challenging task. Collective with its research advancement in flexible sensors, the preparation techniques, performance of the sensor, detailed underlying transduction mechanism, and applications of materials based on flexible sensors with different device structures are reviewed.

Key Points

- Initially, the active materials involved, which play a vital role in deciding the sensor's performance, have been discussed.
- Later, the synthesis and fabrication methodologies utilized to fabricate flexible physical sensors have been discussed.
- Subsequently, the distinctive types of physical sensors, such as piezoresistive, capacitive, piezoelectric, and triboelectric, are explained with detailed transduction mechanisms and comparative studies for evaluation parameters of the fabricated sensors to determine the better physical sensor among the existing literature have been done.
- Lastly, the predominant applications of flexible physical sensors (pressure/strain), followed by a conclusion and future scope in the area of flexible and wearable electronics, are discussed.

Introduction

With the instant change of current society, innovative and upsetting technologies such as the IoT (Internet of Things) and wearable healthcare devices have evolved in recent years, enhancing the well-being and value of life. In the recent past, flexible and wearable physical sensors have engrossed a boundless deal of consideration from researchers around the world as they have inimitable characteristics such as extreme-thinness, lightweight, high flexibility, and stretchability, and also their wide range of potential applications in the field of security, etc., (Hong *et al.*, 2018; Wang *et al.*, 2018, 2017). In comparison to traditional Si (Silicon)-based electronics, flexible electronics have extraordinary malleability to numerous varieties of substrates, be it stiff/soft, twisted/flat. This exceptional benefit has enticed massive research attempts on flexible electronics, and a variety of applications have been established.

Physical (pressure/strain) sensors that alter input pressure/strain into electrical output are a critical member of flexible electronics and have been established into an interdisciplinary area, uniting device and system engineering, signal processing, and material sciences comprising the recently arisen artificial intelligence technologies (Lee *et al.*, 2017; Souri and Bhattacharyya, 2018; Zang *et al.*, 2015). There have been several studies recently to recapitulate the development of flexible pressure sensors. Few of them emphasize flexible electronics, while others are devoted to promising materials (e.g., MXene, graphene-based) for physical sensors (Adepu *et al.*, 2021c; Bokka *et al.*, 2022b; Jiang *et al.*, 2020; Yao *et al.*, 2018). Further, to take the flexible physical sensors technology from lab scale to the actual world, certain vital aspects such as sensor layout, underlying transduction mechanism, and fabrication methodologies are lacking in the earlier reviews. Likewise, how the evolving fabrication methodologies to fabricate highly sensitive physical can influence the area of flexible electronics has not been reviewed.

This review is conceived to deliver a complete picture of the progress of flexible physical (pressure/strain) sensors uniting engineering and scientific developments in this area mutually. Firstly, the active materials involved, which play a crucial role in deciding the sensor's performance, have been discussed. Later, the synthesis and fabrication methodologies utilized to fabricate flexible physical sensors and comparative studies for evaluation parameters of the fabricated sensors to determine the better physical sensor among the existing literature have been done. Subsequently, the distinctive types of physical sensors, such as piezoresistive, piezocapacitive, piezoelectric, triboelectric, etc., are explained with detailed transduction mechanisms. Lastly, the predominant applications of flexible physical sensors, including human-machine interaction, E-skin, healthcare, etc., and future scope in the field of flexible and wearable electronics are shown. An overview of flexible and wearable physical sensors and its applications is displayed in Fig. 1 below.

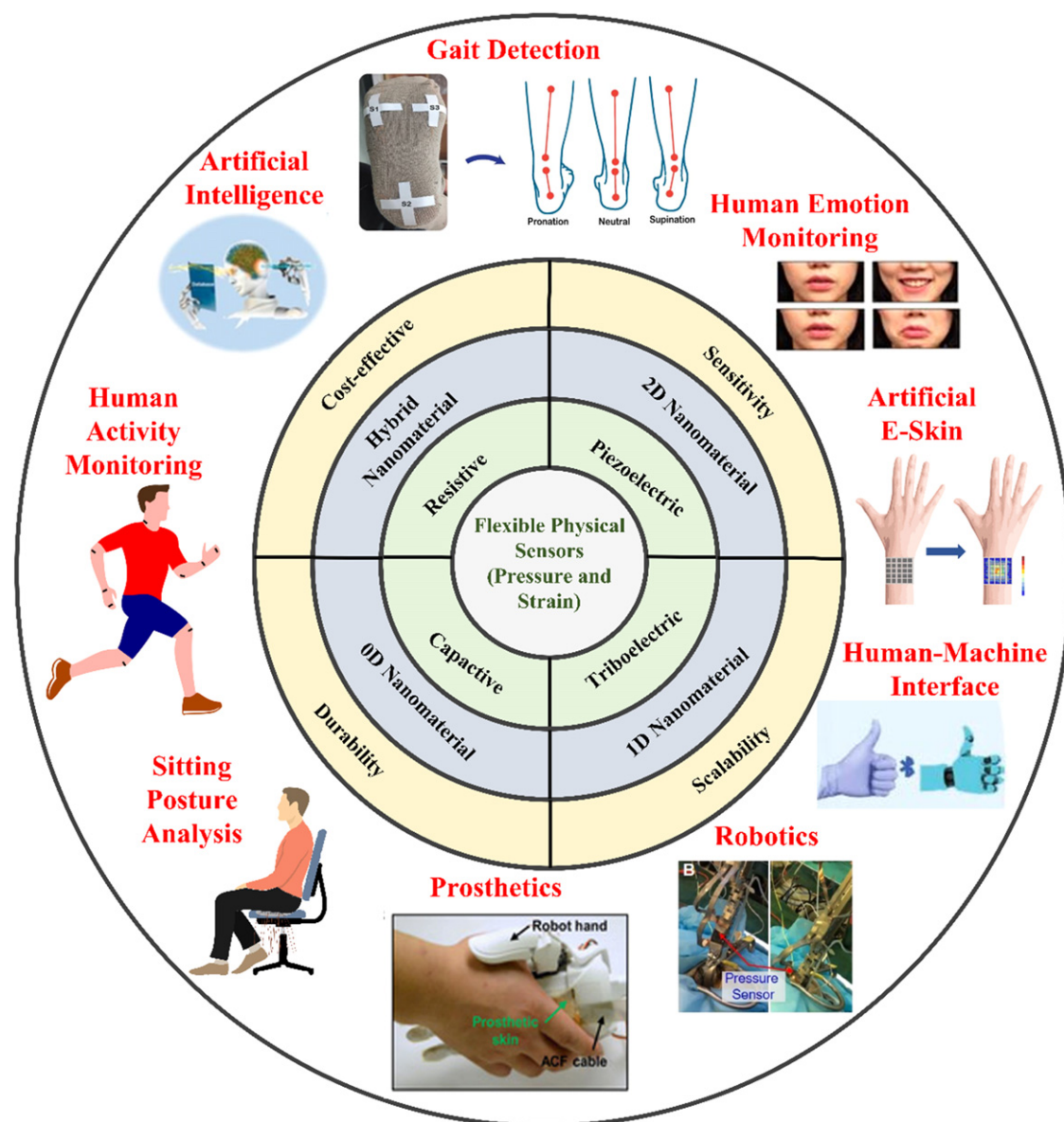


Fig. 1 Overview of flexible physical sensors (pressure/strain); Gait detection: Reproduced with permission from (Kamath, K., Adepu, V., Mattela, V., Sahatiya, P., 2021a. Development of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MoS}_2\text{Se}_{2(1-x)}$ nanohybrid multilayer structures for piezoresistive mechanical transduction. *ACS Appl. Electron. Mater.* 3, 4091–4104) Copyright © 2021, American Chemical Society.; Human Emotion Monitoring: Reproduced with permission from (Roh, E., Hwang, B., Kim, D., Kim, B., Lee, N., 2015. Stretchable, transparent, ultrasensitive, and patchable strain sensor for human-machine interfaces comprising a nanohybrid of carbon nanotubes and conductive elastomers. *ACS Nano* 9, 6252–6261) Copyright © 2015, American Chemical Society; Artificial E-skin and Human Activity Monitoring: Reproduced with permission from (Adepu, V., Mattela, V., Sahatiya, P., 2021b. A remarkably ultra-sensitive large area matrix of MXene based multifunctional physical sensors (pressure, strain, and temperature) for mimicking human skin. *J. Mater. Chem. B* 9, 4523–4534) Copyright © 2021, Royal Society of Chemistry, Human-Machine Interface: Reproduced with permission from (Liu, Z., Zhu, T., Wang, J., *et al.*, 2022. Functionalized fiber-based strain sensors: Pathway to next-generation wearable electronics. *Nano-Micro Lett.* 14, 1–39) Copyright © 2022, Robotics: Reproduced with permission from (Chang, T.H., Tian, Y., Li, C., *et al.*, 2019. Stretchable graphene pressure sensors with Shar-Pei-like hierarchical wrinkles for collision-aware surgical robotics. *ACS Appl. Mater. Interfaces* 11, 10226–10236) Copyright © 2019, American Chemical Society, Prosthetics: Reproduced with permission from (Sim, K., Rao, Z., Zou, Z., *et al.*, 2019. Metal oxide semiconductor nanomembrane-based soft unnoticeable multifunctional electronics for wearable human-machine interfaces. *Sci. Adv.* 5, eaav9653) Copyright © 2019 Cunjiang Yu, Sitting Posture Analysis: Reproduced with permission from (Adepu, V., Kunchur, A., Tathacharya, M., Mattela, V., Sahatiya, P., 2022b. $\text{SnS}/\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) nanohybrid-based wearable electromechanical sensors for sign-to-text translation and sitting posture analysis. *ACS Appl. Electron. Mater.* 4, 1756–1768) Copyright © 2022, American Chemical Society, Artificial Intelligence: Reproduced with permission from (Shi, Q., Dong, B., He, T., *et al.*, 2020. Progress in wearable electronics/photronics – Moving toward the era of artificial intelligence and the internet of things. *InfoMat.* 2, 1131–1162) Copyright © 2020 Chengkuo Lee.

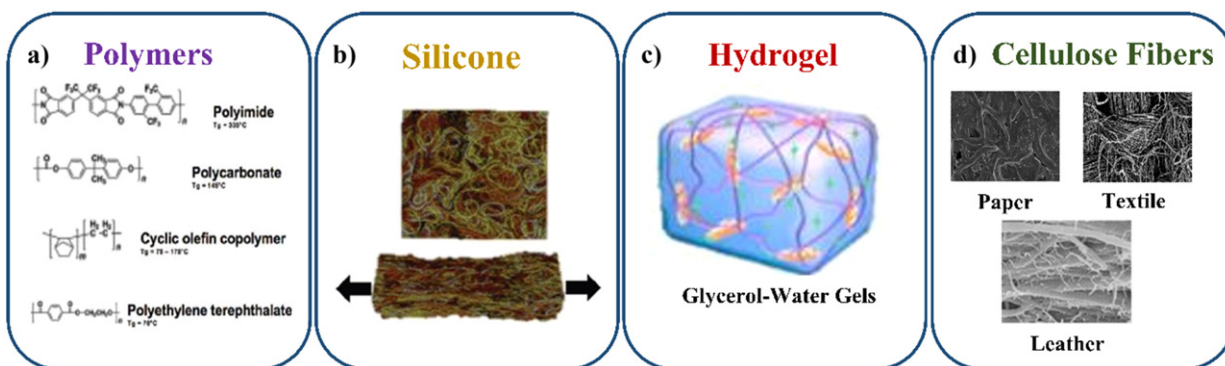


Fig. 2 Materials for flexible physical sensor substrates, (a) General polymer materials by order of glass transition temperatures. (b) Illustration of silicone elastomer based flexible substrates. (c) Graphical illustration of hydrogel. (d) Cellulose fiber-based porous flexible substrates, i.e., paper, textile, and leather. Reproduced with permission from (a) Ni, H., Liu, J., Wang, Z., Yang, S., 2015. A review on colorless and optically transparent polyimide films: Chemistry, process and engineering applications. *J. Ind. Eng. Chem.* 28, 16–27, Copyright © 2015 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved, (b) Root, S.E., Savagatrup, S., Printz, A.D., Rodriguez, D., Lipomi, D.J., 2017. Mechanical properties of organic semiconductors for stretchable, highly flexible, and mechanically robust electronics. *Chem. Rev.* 117, 6467–6499, Copyright © 2017 American Chemical Society, (c) Wei, P., Chen, T., Chen, G., *et al.*, 2020. Conductive self-healing nanocomposite hydrogel skin sensors with antifreezing and thermoresponsive properties. *ACS Appl. Mater. Interfaces* 12, 3068–3079, Copyright © 2020 American Chemical Society, (d) Adepu, V., Kamath, K., Mattela, V., Sahatiya, P., 2021c. Laser-assisted gaussian microstructure patterned PDMS encapsulated $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) based pressure sensor for object and touch detection. *IEEE Sens. J.* 21, 16547–16553, Copyright © 2021 IEEE, FESEM image for textile substrate: Reproduced with permission Adepu, V., Kamath, K., Siddhartha, S., Mattela, V., Sahatiya, P., 2022a. MXene/TMD nanohybrid for the development of smart electronic textiles based on physical electromechanical sensors. *Adv. Mater. Interfaces* 9, 2101687, Copyright © 2022 WILEY-VCH Verlag GmbH & Co.KGaa, Weinheim, FESEM image for leather substrate: Reproduced with permission Zou, B., Chen, Y., Liu, Y., *et al.*, 2019. Repurposed leather with sensing capabilities for multifunctional electronic skin. *Adv. Sci.* 6, 1801283. Copyright © 2019 WILEY-VCH Verlag GmbH & Co.KGaa, Weinheim.

Materials Discussion

Materials for Substrates

The dependency on material composition and properties of the device is regulated by the choice of the substrate employed to fabricate the physical sensor. The structure of each molecule and assembly of the molecules in bulk will determine the physical properties at the molecular scale (Root *et al.*, 2017). Consequently, for a system to bestow stretchability and flexibility, the molecular structures and compositions can be modified by design strategies influenced by various engineering methodologies. To date, various flexible substrates have been used to fabricate flexible physical sensors. Among them, based on the glass-transition temperatures, few of the well-known polymeric materials, i.e., polyimide, PET (polyethylene terephthalate), polycarbonate (Ni *et al.*, 2015), etc., hydrogels (Lin *et al.*, 2016), rubber-like resemblance materials, i.e., silicone elastomers such as Polydimethyl Siloxane (PDMS) have been broadly used owing to simplicity in fabricating flexible sensors and biocompatibility (Khajehsaeid *et al.*, 2013). Also, cellulose fiber-based paper substrates with porous cellulose fibrous matrix (Selamneni *et al.*, 2019; Selamneni *et al.*, 2021a; Selamneni and Sahatiya, 2021; Tobjörk and Österbacka, 2011), textile substrates made of silk, cotton, wool, etc., are utilized to fabricate flexible physical sensors due to ease of availability, minimal cost and highly hygroscopic in nature (Karim *et al.*, 2017; Souri and Bhattacharyya, 2018; Wang *et al.*, 2016). The classification for materials for various flexible substrates utilized to fabricate physical (pressure/strain) sensors is shown in Fig. 2 below.

Active Material Choice and its Synthesis Techniques for Flexible Physical Sensing

The choice of the materials to deposit a thin film on several flexible substrates is discussed in this section. The active material plays a crucial role in fabricating the highly sensitive, flexible physical sensors to improve the performance of the fabricated sensor. In the pursuit of functional nanomaterials for physical sensors, i.e., functional materials to be deposited on the flexible substrates were categorized based on their dimensionalities, such as 2D, 1D, 0D nanomaterials and their hybrid/composites.

2D Nanomaterials

Graphene and its derivatives

In 2004, Novoselov and his group discovered a wonder material named graphene, a 2D layer with one atom thickness, in a pathbreaking scotch tape experiment (Novoselov *et al.*, 2016). This wonder material has exceptional mechanical properties, higher surface area, elevated young's modulus, and remarkable electrical conductivity. All these attributes make certain that graphene and its derivatives have wide-ranging applications in flexible and wearable electronics. The most common and well-known routes to synthesize graphene were chemical reduction, epitaxial growth, mechanical exfoliation, and chemical vapor deposition techniques. (Blake *et al.*, 2007; Deokar *et al.*, 2015). In the recent past, laser-assisted growth has evolved as an assuring technique for synthesizing graphene owing to the easy breakage of

C=O, C-O, or C-N bonds by the intense generation of temperature. Specifically, based on the surface chemical composition and geometry, graphene can be categorized into graphene sheets, graphene ribbon, graphene oxide, and reduced graphene oxide, which can be synthesized using exfoliation and chemical/electrochemical reduction or hydrothermal methods. Graphene sheets have extraordinary electrical properties, while patterning graphene sheets into graphene ribbons can tune their semiconducting properties (Han *et al.*, 2007). rGO has elevated conductivity compared to graphene oxide due to its partially aromated graphitic structure (Huang *et al.*, 2019b; Le *et al.*, 2019; Murugadoss *et al.*, 2019). All these attributes of graphene and its derivatives make specific, prevalent applications in the field of flexible electronics to fabricate flexible physical sensors with improved performance.

Transition metal dichalcogenides and carbides/nitrides

Analogous to graphene, with considerable electrical conductivity, and a larger surface area, transition metal dichalcogenides (TMDs) were discovered in the 2D materials family. Based on these facets, TMDs can be used as a medium for electron transfer and can assist high precision detection in physical sensors (Lan *et al.*, 2019; Yue *et al.*, 2018). The general formula for TMDs is MX_2 , wherein M represents the transition metal, i.e., Mo, W, and X refers to chalcogen, namely O, S, and Se. TMDs with lamellar structure display a broad range of mechanical, chemical, optical, electrical, and thermal properties to sense various physical parameters such as pressure and strain effectively, and these 2D TMD materials are synthesized using various methods such as CVD, hydrothermal, chemical interaction, solvent exfoliation, etc. (Kolli *et al.*, 2022; Yin *et al.*, 2021). Besides these synthesis techniques, recently, a laser-assisted chemical reduction technique was also utilized to synthesize TMDs nanosheets.

MXene has the chemical formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$ in which M refers to the transition metal, X represents C or N, and T_x refers to surface functional groups such as O, F, and -OH. To date, about 60 possible combinations of MXene, including Ti_3C_2 , V_2C , and Ti_2N , have been reported (Gogotsi and Anasori, 2019; Kim *et al.*, 2021). The extraordinary electrical conductivity, hydrophilicity, and superior ion transport properties of MXenes synthesized by a very well-known chemical etching technique have exhibited a phenomenal impact in the field of flexible and wearable electronics to utilize them as excellent materials for the fabrication of physical sensors (Adepu *et al.*, 2021c; Gogotsi and Huang, 2021). Initially, HF was used as an etchant to chemically etch the existing metallic bond of MAX to synthesize the accordion shape layered MXene (Alhabeb *et al.*, 2017). Later, in 2011 Ghidui and co-workers synthesized highly conducting MXene with elevated electrical conductivity in comparison to the conventional HF etching method by utilizing a mixture of LiF and HCl as etchant (i.e., MILD method) to synthesize layered MXene with finite interlayer spacing that has shown excellent physical sensing capabilities upon application of external stimuli on to the fabricated physical sensor (Ghidui *et al.*, 2014). Also, these MXenes owing to excellent biocompatibility and high accuracy detection capabilities based on the aforementioned properties, were found as prospective candidates for flexible physical sensing applications (Chen *et al.*, 2018).

1D nanomaterials

CNTs (Carbon Nanotubes)

One-dimensional cylindrical structures with superior aspect ratio and electron mobility which are known as carbon nanotubes, have been treated as a perfect material for flexible and wearable physical sensors owing to exciting properties such as elevated intrinsic carrier mobility ($\sim 10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (Zhou *et al.*, 2005), high electrical conductivity ($\sim 10^4 \text{ S cm}^{-1}$) (Zeng *et al.*, 2014), extraordinary mechanical performance (i.e., the elastic modulus is equal to (~ 1 Tera pascals)), high flexibility and chemical stability (Hammock *et al.*, 2013; De Volder *et al.*, 2013). Techniques, namely arc discharge, CVD, and laser ablation, are used to synthesize CNTs utilizing methane (CH_4), ethylene (C_2H_4), or acetylene (C_2H_2) as a source of carbon. The length, orientation, and diameter of the attained nanotube can be controlled using these techniques. Furthermore, these synthesized CNTs can be transferred onto various flexible substrates, such as spin coating, vacuum filtration, etc., to fabricate numerous flexible physical (strain) sensors for human-machine interaction applications (Sajid *et al.*, 2016; Wang *et al.*, 2016).

Metal nanowires

Ultrathin metallic nanowires containing exceptional conductivity and strong, flexible mechanical properties were considered unique building blocks for the fabrication of physical sensors. Metal nanowires such as Cu, Ag, and Au nanowires are extensively used in the field of wearable electronics as wearable physical sensors. These nanowires were usually synthesized by employing a chemical reduction route by reducing metal precursor materials (e.g.:Ag nanowires are synthesized by chemical reduction of AgNO_3) (Sun *et al.*, 2002). With specific conditions and also by utilizing CTAB, PVP, and polyol as capping agent (Zhang *et al.*, 2017), reducing agent (Sun *et al.*, 2002), and soft template (Wang *et al.*, 2015). Also, there are several other reducing agents are utilized to synthesize the metal nanowires. Kim and co-workers synthesized the Cu nanowires by utilizing the WS_2 nanosheets as a reducing agent. Specifically, the Cu ions are adsorbed physically into WS_2 nanosheets and reduced to Cu NWs, and also the diameter of the synthesized nanowires can be controlled using this technique (Kim *et al.*, 2020). The role of these synthesized metallic nanowires in flexible and wearable physical sensors is similar to that of CNTs mentioned above. (Lan *et al.*, 2019).

0D nanomaterials

Zero dimensional materials typically comprise of C_{60} , metal nanoparticles, quantum dots, etc. Out of them, metal nanoparticles were highly utilized as 0D nanomaterials for fabricating physical sensors due to air stability and the easiness to change their characteristics and size/shape/composition. The size-related optical, electronic, and magnetic properties, i.e., quantum-size effect, make it appealing for utilization in distinct applications. Also, the remarkable electrical conductivity and large specific surface area of metal nanoparticles can assist in synthesizing on various flexible substrates, which further helps to enhance the sensitivity of the fabricated physical sensor. Seed-

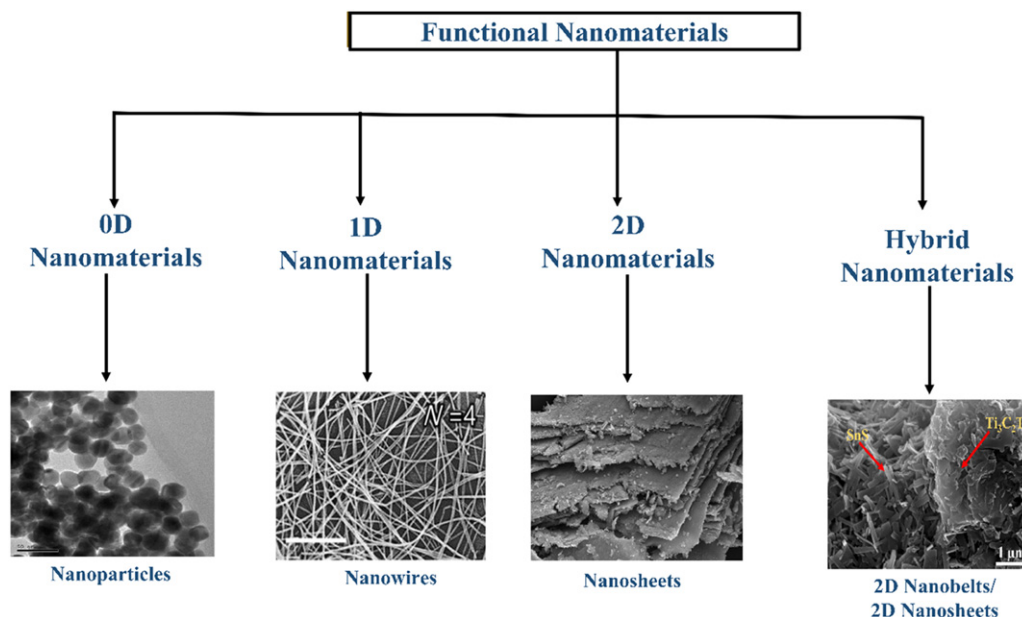


Fig. 3 Classification of functional nanomaterials based on dimensions; TEM Image of Nanoparticles: Reproduced with permission (Zhang, W., Liu, Q., Chen, P., 2018. Flexible strain sensor based on carbon black/silver nanoparticles composite for human motion detection. *Materials (Basel)*. 11, 1836) Copyright © 2018 by the Weiye Zhang, Qiang Liu, and Peng Chen; FESEM Image of Nanowires: Reproduced with permission (Jo, H.S., An, S., Park, C.W., *et al.*, 2019. Wearable, stretchable, transparent all-in-one soft sensor formed from supersonically sprayed silver nanowires. *ACS Appl. Mater. Interfaces* 11, 40232–40242) Copyright © 2019 American Chemical Society; FESEM Image of Nanosheets: Reproduced with permission (Bokka, N., Adepu, V., Sahatiya, P., 2022a. Sublimation of MXene/camphor device: A study on self – Destructive dry transiency. *Mater. Adv.* 3, 1272–1279) Copyright ©2022 Royal Society of Chemistry; FESEM Image of 2D Nanobelts/2D Nanosheets: Reproduced with permission (Adepu, V., Kunchur, A., Tathacharya, M., Mattela, V., Sahatiya, P., 2022b. SnS/Ti₃C₂T_x (MXene) nanohybrid-based wearable electromechanical sensors for sign-to-text translation and sitting posture analysis. *ACS Appl. Electron. Mater.* 4, 1756–1768) Copyright ©2022 American Chemical Society.

mediated growth and chemical reduction were well-known methods to synthesize 0D metal nanoparticles (Huo *et al.*, 2019). In the recent past, Yao and coworkers intended an attempt to synthesize noble metal nanoparticles by utilizing flexible metallic MoS₂ paper as an alternative to a conventional reducing agent. This new methodology understands the instinctive synthesis of noble metal nanoparticles by in-situ redox reaction among the precursor solution used (i.e., PdCl₂, RuCl₃, etc.) of metal nanoparticles (i.e., Pd, Ru, etc.) and MoS₂ nanosheets at normal atmospheric conditions and enhanced efficiency (Yao *et al.*, 2020). Likewise, microorganism aided technique is considered as sustained route to synthesize 0D nanomaterial synthesis (Salunke *et al.*, 2016).

Hybrid nanomaterials

The role of hybrid nanomaterials is similar to that of pristine nanomaterials discussed above to improve the performance of a flexible physical sensor. The hybrid nanomaterials can be specifically used to enhance further electron transport, which improves electrical conductivity and which, in turn, enhances the performance of the fabricated flexible physical sensor. Also, these hybrid nanomaterials offer a solution to Cu nanomaterials oxidation issues and biocompatibility problems of Ag nanomaterials.

Among various hybrid/composite nanomaterials, core-shell nanocomposites were mainly used to fabricate flexible physical sensors. Core-shell nanocomposites are usually synthesized by utilizing a replacement reaction, in which the issues ensued by the shell can be overcome by the core in the nanocomposite. Recently, 2D/2D, 2D/1D, 2D/0D nanohybrids (e.g., MXene/TMD, TMD/Nanotubes, MXene/Nanoparticles, etc.) were also utilized to improve the performance of the as-fabricated physical sensors owing to synergistic effect occurring at the interface of two materials (Adepu *et al.*, 2022a,b). In this regard, there is a considerable demand for nanohybrids in the field of flexible and wearable electronics. The schematic illustration for the classification of nanomaterials based on the dimensions is depicted in Fig. 3 below.

Fabrication Methodologies/Strategies

The increasing demand for flexible and wearable physical sensors has led to significant trials and quick improvements in fabricating them. Several manufacturing methods have been utilized to fabricate numerous physical sensors in this perspective. These fabrication strategies are categorized into two types (1) compositing materials and (2) pattern transferring. This section discusses the most common and essential fabrication methodologies of physical sensors.

Blending various materials into a composite is the easiest fabrication tactic. In this approach, the functional materials are doped into polymers by ultrasonication/magnetic stirring, and later dried flexible composites can be made in either

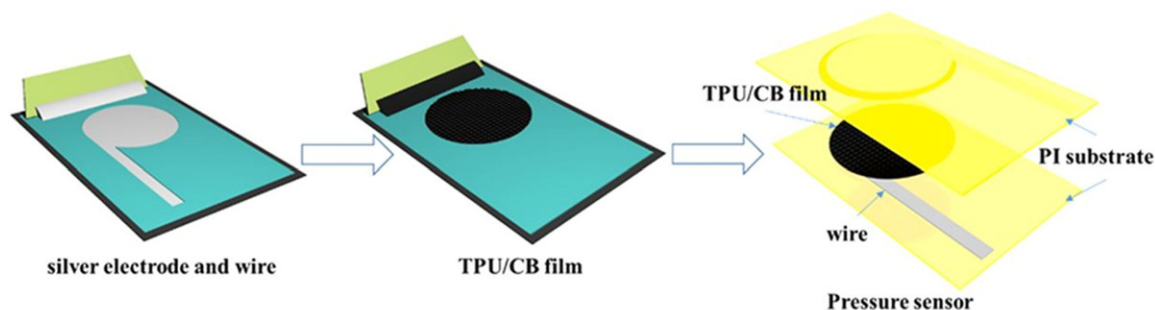


Fig. 4 Schematic illustration for the Thermoplastic polyurethane/carbon black-based pressure sensor fabrication process by screen printing technique. Reproduced with permission from Jiang, S., Yu, J., Xiao, Y., Zhu, Y., Zhang, W., 2019. Ultrawide sensing range and highly sensitive flexible pressure sensor based on a percolative thin film with a knoll-like microstructured surface. *ACS Appl. Mater. Interfaces* 11, 20500–20508, Copyright © 2019 American Chemical Society.

bulk/film type to satisfy application constraints. These mixed composites have complicated electromechanical characteristics engendered by the assortment of polymer substrates and fillers and the considerable reliance on doping concentration and dissemination state. Carbon black-silicone composite is a typical case in which filler concentration plays a significant role in physical sensing. The electrical resistance of the fabricated pressure sensor increases upon application of external uniaxial pressure when carbon black's concentration is low and decreases when the carbon black's concentration is high (Luheng *et al.*, 2009). Specifically, it is evident that the filler's dimensionality also influences the composites' electro-mechanical properties. Also, the encapsulation technique also produces sensitive composites, wherein the active material is crammed between substrates to make the substrate-sensitive composite-substrate structure.

A well-known fabrication method can obtain the desired geometries of flexible physical sensors using pattern transferring. The existing techniques primarily include but are not restricted to microscale modeling, handwriting, printing (i.e., 3D printing, inkjet printing, and screen printing), and lithography.

Microscale modeling is frequently employed to make the microstructure in substrates, sensing combinations, and electrodes. The attained components can be utilized to improve the measurement sensitivity of capacitive and piezoresistive type physical sensors by the notions of gap alignment and microstructure dielectric. Lithography is another pattern transporting process to recognize distinct and effective geometries in the field of flexible electronics. In this method, the first functional layer is deposited onto the substrate and then scrapes the unsought areas using reagent solutions by photolithography. Due to the extreme accuracy of wet etching and photolithography, the realized devices can acquire incredibly advanced geometries and strong utility.

Another technique for fabricating physical sensors is screen printing, wherein the standard mask is utilized to print the synthesized functional material on the desired substrate surface using a fill blade. The functional material remains on the substrate by forming a patterned film as the mask goes away. Zhang *et al.* fabricated a Thermoplastic Polyurethane /Carbon Black slurry-based flexible pressure sensor by employing a screen printing technique (Jiang *et al.*, 2019) which is illustrated in Fig. 4 below.

Fabrication of flexible physical sensors at a low cost is critical. The below-mentioned works demonstrate the simple techniques utilized to develop low-cost, flexible sensors in a facile method.

Sahatiya *et al.* fabricated an Eraser-based eco-friendly skin-like large-area matrix of flexible carbon nanotube strain and pressure sensors (Sahatiya and Badhulika, 2016). The Schematic of the sensor fabrication is shown in Fig. 5 below.

Recently, Iqra *et al.* (2022). have developed a low-cost piezoresistive strain sensor using reduced graphene oxide on PDMS. The reduction was performed using a technique called laser scribing. The schematics of the fabrication procedure is displayed in Fig. 6 below.

Furthermore, there are various other fabrication techniques besides the one mentioned and discussed above to develop a Flexible physical sensor. Specifically, in a few of the methods, direct growth/deposition of sensing material on a flexible substrate is not possible. In such cases, fabricating flexible sensors is achieved through a 2-step process: The first step is synthesizing the active sensing material, and the next step is transferring the prepared active sensing material onto a flexible substrate. Furthermore, research is being carried out to fabricate flexible physical sensors through a facile method to overcome the aforementioned limitations.

Different Types of Pressure/Strain Sensors Sensing Mechanisms

Physical (Pressure and Strain) sensors can be classified based on their working mechanisms. Piezoresistive, piezoelectric, triboelectric, and capacitive type physical sensors will be discussed in this section.

Piezoresistive

The piezoresistive physical sensors work based on the resistance change occurring in the device when a mechanical strain or pressure is applied. The resistance can be obtained by equation $R = \rho * l/A$, in which ρ is the material's resistivity, and l and A are the length

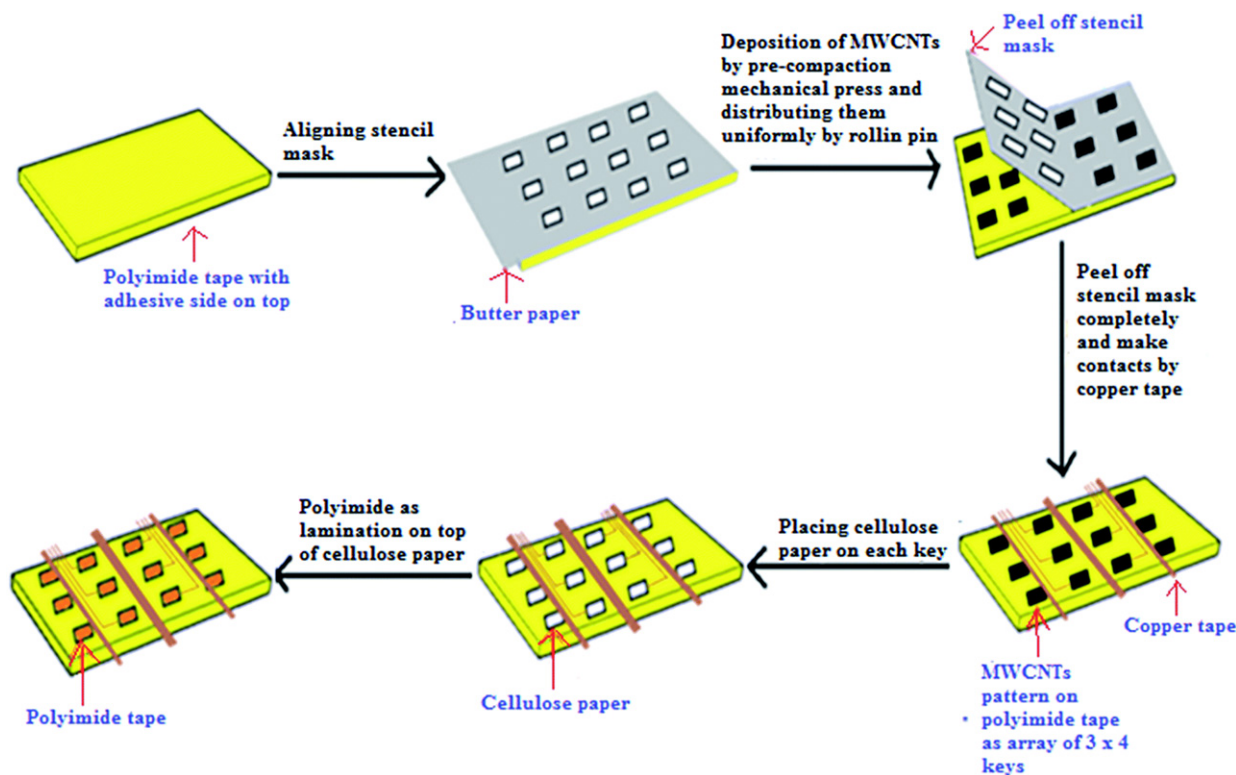


Fig. 5 Schematic showing the steps involved in the development of the Strain sensor. Reproduced with permission from Sahatiya, P., Badhulika, S., 2016. Solvent-free fabrication of multi-walled carbon nanotube based flexible pressure sensors for ultra-sensitive touch pad and electronic skin applications. *RSC Adv.* 6, 95836–95845, Copyright © 2016 Royal Society of Chemistry.

of the conductor and cross-sectional area. The resistance variation for specific materials is primarily owing to inherent resistivity alter upon deformation and for some additional materials depends on the alteration of geometrical parameters (i.e., l , A). In total, the resistive physical sensors mechanism is summarized as (1) alterations in intrinsic resistance and (2) contact resistance changes.

The alterations in the intrinsic resistance predominantly derive from the alteration of electronic band structure for the duration of deformation, that can be noticed in numerous materials (i.e., graphene (Bae *et al.*, 2013), MXene (Sindhu *et al.*, 2022), CNTs (carbon nanotubes) (Tombler *et al.*, 2000)). On the basis of the transfer of holes and mass shift conduction owing to applied stress, the variation in semiconductor's resistance has been extensively used in mechanical sensors (Edwards and Beaulieu, 1969; Toriyama and Sugiyama, 2002). Also, the sensing performance is notably affected by the structure of the material.

The variations in the contact resistance might derive from variations in the conductive material's density, the contact area, and the conductive path generated by distortion. Under the mechanical stimuli, the R_c varies more substantially than the intrinsic resistance and thus leads the sensitivity. Most contact resistive-type mechanical sensors have a negative resistive effect, which implies a reduction in resistance as the pressure increases.

The Schematic for a piezoresistive MXene-based pressure sensor's working mechanism explained by Ma.Y. and his group is depicted in Fig. 7.

Capacitive

The applied external mechanical stimuli get converted into capacitance changes in capacitive type physical sensors. The capacitance (C) of a capacitor can be estimated using the equation, i.e., $C = \epsilon_r A / 4\pi k d$, in which ϵ_r is relative permittivity, A is the actual overlap area, k is electrostatic constant, d is the distance amongst electrodes. Specifically, d is susceptible to normal forces, and A is susceptible to tensile strain and shear forces (Boutry *et al.*, 2018; Lipomi *et al.*, 2011). Capacitive physical sensors have the benefits of elevated sensitivity, minimal power utilization, and improved temperature independence. On the contrary, a capacitive type physical sensor's sensitivity is constrained by A , and it is distinctly diminished as the device's size reduces. Also, further fabricating the capacitive type physical sensor with large sensitivity stays difficult.

The capacitive type sensors usually comprise a dielectric layer crammed with two electrodes. In this context, to improve the sensitivity of these types of sensors, low modulus dielectrics (e.g., Ecoflex, PDMS, etc.) are frequently utilized to enhance the sensitivity of fabricated sensors owing to their large deformation. Nevertheless, owing to the incompressible and viscoelastic of the elastomeric dielectrics, the response time and sensitivity of the capacitive type physical sensors are yet challenging. To deal with this confront, researchers around the world created dielectric materials with microstructures (i.e., micro pyramids (Adepu *et al.*, 2021c), pores (Zhu *et al.*, 2018), beads (Kim

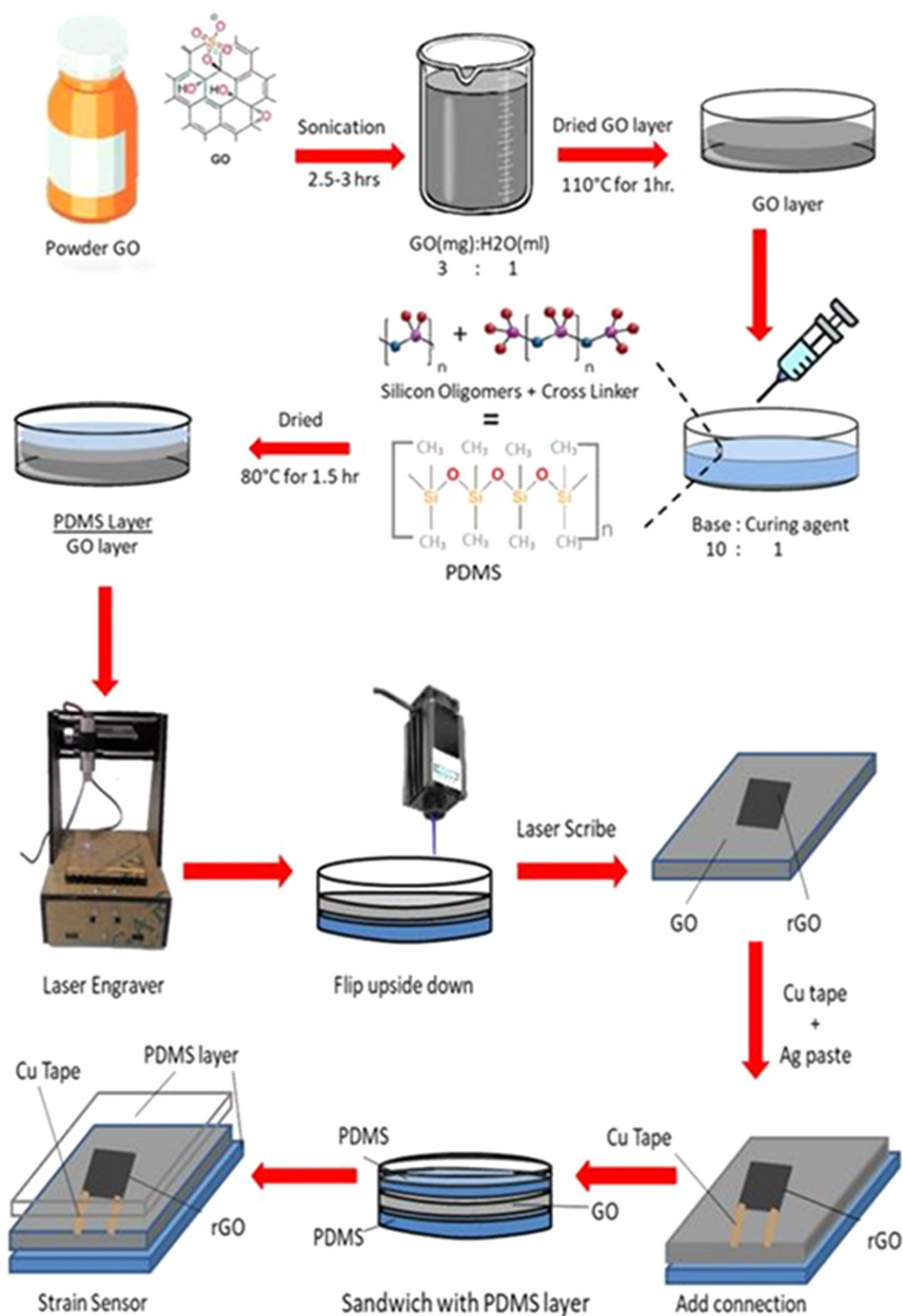


Fig. 6 Fabrication of piezoresistive strain sensor using laser scribing. Reproduced with permission Iqra, M., Anwar, F., Jan, R., Mohammad, M. A., 2022. A flexible piezoresistive strain sensor based on laser scribed graphene oxide on polydimethylsiloxane. Sci. Rep. 12, 4882, Copyright © 2022, The Maham Iqra.

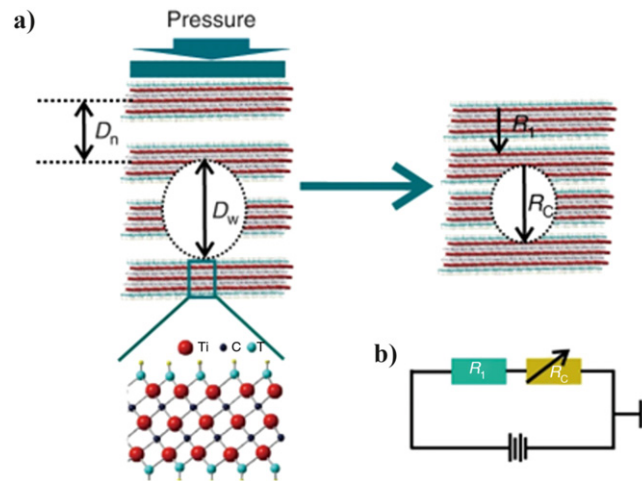


Fig. 7 (a) Working mechanism of MXene material based Piezoresistive sensor, and (b) circuit diagram of the piezoresistive sensor. Reproduced with permission Ma, Y., Liu, N., Li, L., *et al.*, 2017. A highly flexible and sensitive piezoresistive sensor based on MXene with greatly changed interlayer distances. *Nat. Commun.* 8, 1–7, Copyright © 2017, The Yihua Gao.

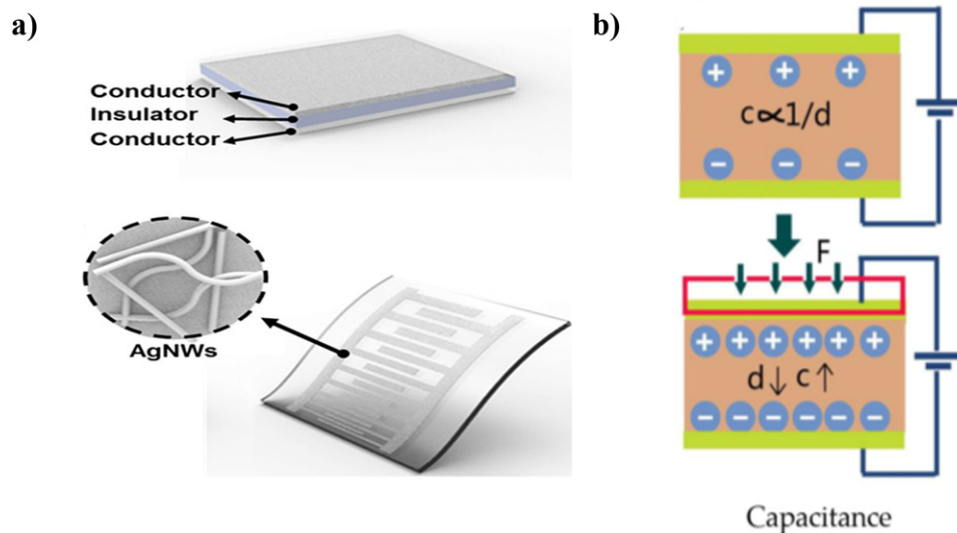


Fig. 8 (a) Piezo-capacitive sensor developed from Ag Nanowires, (b) transduction mechanism of capacitive type sensor. Reproduced with permission from Xu, F., Li, X., Shi, Y., *et al.*, 2018. Recent developments for flexible pressure sensors: A review. *Micromachines* 9, 580, Copyrights © 2018, The Ruping Liu.

et al., 2018a), cylinders (Zhu *et al.*, 2018), etc.). The schematic illustration for the working mechanism of the capacitive type sensor is displayed below in Fig. 8(b). The capacitive-based physical sensor device using Ag nanowires employed for human motion monitoring developed by Kim and his co-workers (Kim *et al.*, 2017) is displayed in Fig. 8.

Piezoelectric

The piezoelectric electromechanical sensors can translate dynamic pressures into electrical signals utilizing piezoelectric materials with benefits of enhanced sensitivity and quick response that are extensively used in dynamic monitoring (Yu *et al.*, 2016). The longitudinal separation of applied force produced positive and negative charges, caused by the reorganization of dipoles, known as the piezoelectric effect (Hu *et al.*, 2018). The piezoelectric effect intensity is understood by the equation $q = d_{33}F$, in which F is the force applied, and d_{33} is the piezoelectric strain constant. In comparison to capacitive and resistive type physical sensors, these piezoelectric effect-based sensors are observed self-powered and have more extensive application possibilities. Persano and his co-workers utilized the aligned arrays of PVDF-TrFE and engineered a self-powered large-area flexible sensor with improved sensitivity also at considerably small pressures (Persano *et al.*, 2013). Further, the pyroelectric effects contain piezoelectric materials. Piezoelectric electromechanical sensors need to serve the challenge of

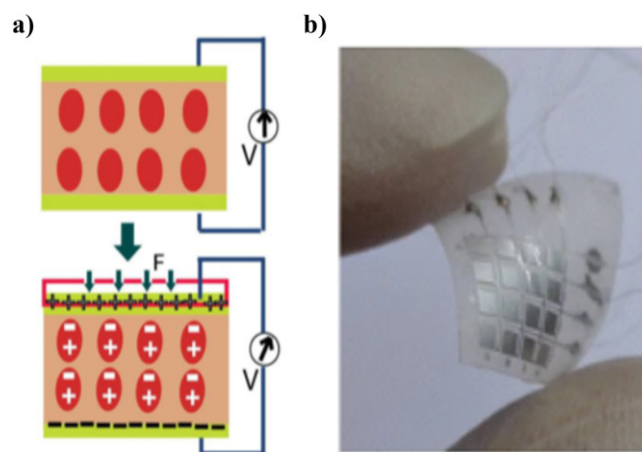


Fig. 9 (a) Piezoelectric transduction mechanism (2018) Micromachines, (b) strain sensor based on PVDF piezoelectric film. Reproduced with permission from (a) and (b) Xu, F., Li, X., Shi, Y., *et al.*, 2018. Recent developments for flexible pressure sensors: A review. Micromachines 9, 580, Copyright © 2018, The Ruping Liu and Copyright © 2018, The Bin Yu.

thermal interference. In this context, wang and his co-workers revealed a different device structure consisting of a capacitor and single-electrode piezoelectric generator. The input piezoelectric signal was altered into a square wave by a capacitor was recognized the pyroelectric pulse signal. So, this device, based on a piezoelectric mechanism, was concurrently utilized to detect pressure and temperature (Wang *et al.*, 2018). Also, due to the generation of impulsive output signals, static sensing is inappropriate for using piezoelectric-type physical sensors. Therefore, static pressure measurements in a simple manner is one of the critical challenges for piezoelectric type physical sensors. A schematic showing the transduction mechanism in the piezoelectric physical sensor is given in Fig. 9(a). And a digital image of a flexible piezoelectric strain sensor based on PVDF polymer developed by Lu and his group using a piezoelectric mechanism is displayed in Fig. 9(b).

Triboelectric

The triboelectric physical sensor is a sort of innovative self-powered sensor that induces a mechanical signal into an electrical signal via. Triboelectric effects. Analogous to piezoelectric type sensors, triboelectric type sensors create electrical signals only at the instant of contact and split. So, the triboelectric type sensors are most appropriate for dynamic sensing. In the recent past, triboelectric nanogenerators (TENG) have been among the most extensively explored triboelectric type physical sensors. In 2012, Wang *et al.* demonstrated the first transparent TENG for a self-powered pressure sensor (Fan *et al.*, 2012). The TENG can be classified into 4 working modes of operation, (i) free-standing mode, (ii) vertical-contact separation mode, (iii) lateral sliding mode, and (iv) single-electron mode (Wang *et al.*, 2015a). Out of them, single-electron mode and vertical-contact separation modes are almost common modes in the physical sensor. The magnitude and frequency of mechanical stimuli influence the output performance of the fabricated TENG (Lin *et al.*, 2013; Wang *et al.*, 2015b). Jin *et al.* (2017) have developed a Triboelectric Nanogenerator finger movement monitoring sensor (self-powered). Also, the digital image of the developed sensor and its working mechanism is displayed in Fig. 10.

Based on the synthesis and fabrication techniques utilized to fabricate various physical sensors with distinct underlying transduction mechanisms, a detailed comparison to find out the highly sensitive physical sensor was tabulated in Table 1 below.

From the above literature, it is clearly evident that the highest value for the sensitivity of the existing fabricated pressure sensors in the literature was found to be $\sim 200 \text{ kPa}^{-1}$ with piezocapacitive mechanism (PVA/H₃PO₄ functional material deposit on polyimide substrate) and maximum value of gauge factor for fabricated strain sensors to-date was found to be ~ 1344.1 with piezoresistive mechanism (CNT ink functional material deposit on PU yarn). And still, there is tremendous scope for the fabrication of highly sensitive and flexible physical sensors for utilizing them in real-time applications.

Applications

Pressure Sensor Applications

Over the last two decades, demand for flexible pressure sensors has been rapidly increasing due to their wide variety of applications, including human-machine interface, next-generation personal health care monitoring devices, robotics, skin electronics, and human motion monitoring, etc. (Huang *et al.*, 2019a; Mishra *et al.*, 2021; Yang *et al.*, 2022).

Human-machine interface

Devices and software installed on machines that aid human-machine communication are called human-machine interfaces. A significant part of interpreting mechanical input from humans into electrical signals for regulating the machine or offering

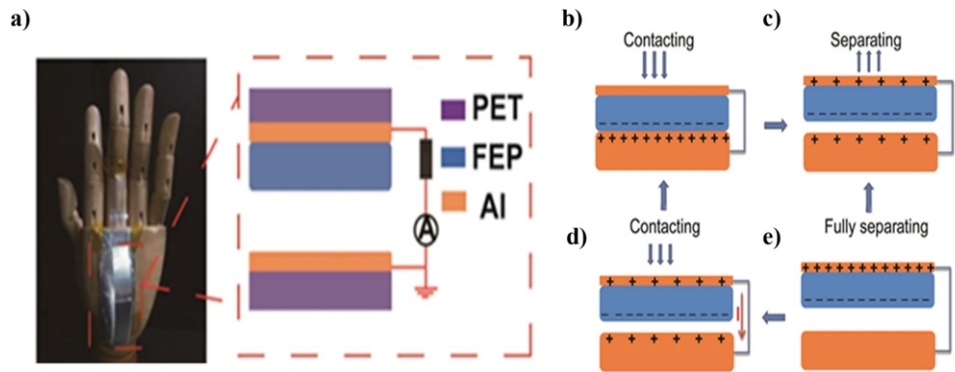


Fig. 10 (a) Triboelectric nanogenerator (TENG) developed using PET substrate, FEP, and Al as friction materials, (b–e) sensing principles. Reproduced with permission from Jin, L., Tao, J., Bao, R., Sun, L., Pan, C., 2017. Self-powered real-time movement monitoring sensor using triboelectric nanogenerator technology. *Sci. Rep.* 7, 1–6, Copyrights © 2017, Caofeng Pan.

feedback can be done by flexible pressure sensors. For example, *Kim et al.* demonstrated an extremely stretchable, transparent, and wearable iconic touch panel to play music and chess, write words and the fabricated touch panel can be used under $> 1000\%$ strain (*Kim et al.*, 2016). Recently *Selamneni et al.* fabricated an SnS/paper-based pressure sensor with a sensitivity of $\sim 3.18 \text{ kPa}^{-1}$ and demonstrated the tracking of the index finger trajectory on the prepared 3×3 pressure sensor array, as shown in *Fig. 11(a)* (*Selamneni et al.*, 2021a). Furthermore, pressure sensors can be used for security applications, including smart floor sensors sign to text translation (*Adepu et al.*, 2022b; *Selamneni et al.*, 2021b).

E-skin applications

Flexible electronics with various sensing capabilities that mimic human skin, but are not limited to human skin, are referred to as e-skin (electronic skin) (*Yang et al.*, 2019; *Huang et al.*, 2019a). E-skin has several practical applications, such as detecting unknown objects, restoring the sensing abilities of physically challenged people, robotics, etc. (*Yang et al.*, 2019). E-skin often requires the use of multiple functional electronic components. Sensors, flexible power supplies, and transmission and processing components are commonly utilized functional components for the fabrication of e-skin. *Park et al.* (2019) demonstrated a flexible, large-area, and ultrathin MoS_2 based tactile sensors driven by an active-matrix circuitry and utilized it for detecting/mapping the unknown object shape by integrating it on the palm of a human hand, as shown in *Fig. 11(b)*. Recently *Zheng et al.* (2021) fabricated an MXene/cotton fabric based pressure sensor, and it was utilized for a smart e-skin demonstration, as displayed in *Fig. 11(c)*.

Health care applications

Flexible pressure sensors are widely used in health care applications to monitor several vital signs of the human body, such as pulse monitoring, heart rate, and voice recognition. Gait detection is critical for detecting the early stage of foot disorders, neurological disorders, and parkinsonian dementias (*Vergheze et al.*, 2002). *Krutarth et al.* demonstrated a piezoresistive pressure sensor based on $\text{Ti}_3\text{C}_2\text{Tx}/\text{MoS}_2\text{xSe}_{2(1-x)}$ and used for real-time monitoring of gait detection. The fabricated pressure sensor was integrated on foot, as seen in *Fig. 12(a)* shows the change in the device current was monitored to access the different gaits (*Kamath et al.*, 2021). Recently, *Adepu et al.* developed a prototype for a smart bed for sleep monitoring using fabricated $\text{Ti}_3\text{C}_2\text{Tx}/\text{NiSe}_2$ based flexible pressure sensors. A dedicated android application was developed for diagnosis purposes to monitor the real-time sensor data, as shown in *Fig. 12(b)* (*Adepu et al.*, 2021a). *Yue et al.* (2018) developed an MXene-sponge-based highly sensitive pressure sensor and utilized it for real-time monitoring of human physiological signals, arterial pulse monitoring, and throat muscle movement, as shown in *Fig. 12(c)*.

Strain Sensor Applications

With the increasing demand for wearable electronics, flexible and stretchable strain sensors occupy a significant role in the flexible and wearable electronics industry. The numerous applications of strain sensors are briefly explained below.

Human motion monitoring

Flexible strain sensors are essential for human health care monitoring owing to their continuously detecting a wide range of human body joints ranging from large joint motion detection to minute deformations identification (*Souri et al.*, 2020). The subtle deformation in body movements and exact signal variation can be identified by using highly sensitive flexible strain sensors. *Fig. 13* demonstrates human motion monitoring by attaching a strain sensor to the human body. The current variations were observed by changing the bending angle of different body joints of the human body. *Fig. 13(a)* shows the strain sensor affixed to the human finger, where the temporal response (current) was enhanced by increasing the strain (i.e., increasing the bending angle). Similarly, the same trend was continued by the inclusion of strain sensor on the elbow and wrist, at various bending degrees, the device current changes proportionately, as depicted in *Fig. 13(b, c)* (*Adepu et al.*, 2021b). In another study, a strain

Table 1 Comparison of the fabricated physical sensors using various functional nanomaterials

Functional nano-material	Substrate	Fabrication method	Sensing mechanism	Type of physical sensor	Sensitivity	Gauge factor	References
CNT Fiber	Ecoflex	Dry CVD	Piezo-resistive	Strain	–	48($\epsilon \sim 400\%$ –700%)	(Kim <i>et al.</i> , 2015)
Ag NWs	PDMS	Drop casting and Peeling	Piezo-resistive	Strain	–	14($\epsilon \sim 70\%$)	(Amjadi <i>et al.</i> , 2014)
ZnO NW array	PET	Hydrothermal	Piezo-electric	Strain	–	1813	(Zhang <i>et al.</i> , 2014)
MXene Film	Polyimide	Inkjet printing and Drop casting	Piezo-resistive	Pressure	180 kPa ⁻¹ (~ 40 kPa)	–	(Ma <i>et al.</i> , 2017)
Polyimide/Graphene foam	Acrylic bar	Freeze drying and thermal annealing	Tribo-electric	Pressure	0.52 N ⁻¹ (~ 30 N)	–	(Zhao <i>et al.</i> , 2019)
Micro-structured graphene	PDMS	Spray Coating and assembling	Piezo-resistive	Pressure	1.2 kPa ⁻¹ (~ 30 kPa)	–	(Shi <i>et al.</i> , 2018)
MoS ₂ /GPN/Ecoflex	Ecoflex	TCVD and thermal decomposition	Piezo-resistive	Pressure and strain	6.06 kPa ⁻¹ (~ 25.4 kPa)	24.1($\epsilon \sim 50\%$)	(Kim <i>et al.</i> , 2018b)
CaCu ₃ Ti ₄ O ₁₂ - PDMS	PDMS	Electro-spinning and porogen assisted process	Piezo-capacitive	Pressure	1.66 kPa ⁻¹ (~ 0.64 kPa)	–	(Mu <i>et al.</i> , 2018)
SSNPs	PET	Spin coating	Piezo-resistive	Pressure	2.46 kPa ⁻¹ (~ 16.3 kPa)	–	(Lee <i>et al.</i> , 2016)
Ti ₃ C ₂ T _x	PU Foam	Dip coating	Piezo-resistive	Pressure and strain	34.24 kPa ⁻¹ (~ 3.185 kPa)	323.59($\sim 20\%$)	(Adepu <i>et al.</i> , 2021b)
Ti ₃ C ₂ T _x /CNT	Latex rubber	Air spray coating	Piezo-resistive	Strain	–	772.6($\sim 70\%$)	(Cai <i>et al.</i> , 2018)
CNT ink	PU Yarn	Swelling and Sonication	Piezo-resistive	Strain	–	1344.1($\sim 200\%$)	(Sun <i>et al.</i> , 2019)
PVA/H ₃ PO ₄	polyimide	E-beam evaporation and spin coating	Piezo-capacitive	Pressure	200 kPa ⁻¹ (~ 320 kPa)	–	(Bai <i>et al.</i> , 2020)
rGO	PET	Drop casting	Piezo-resistive	Pressure	178.5 kPa ⁻¹ (~ 42 Pa)	–	(Jia <i>et al.</i> , 2019)
Nested wrinkling PPy	PDMS	Chemical oxidation polymerization	Piezo-resistive	Pressure	19.32 kPa ⁻¹ (~ 2.036 kPa)	–	(Yang <i>et al.</i> , 2018)
Ti ₃ C ₂ T _x /SnSe ₂	Cotton	Dip coating and hydro-thermal	Piezo-resistive	Pressure and strain	14.959 kPa ⁻¹ (~ 3.185 kPa)	14.108	(Adepu <i>et al.</i> , 2022a)
Ti ₃ C ₂ T _x /MoS ₂ xSe ₂ (1–x)	Cellulose paper	Vacuum filtration and dip coating	Piezo-resistive	Pressure and strain	13.43kPa ⁻¹ (~ 3.185 kPa)	3.51($\sim 25\%$)	(Kamath <i>et al.</i> , 2021)
CNT/PDMS composite	PDMS	Spray deposition and Printing	Piezo-resistive	Strain	–	35($\sim 45\%$)	(Wang <i>et al.</i> , 2018)
Graphene nanosheets/Au film/ Graphene nanosheets	PU Yarn	Layer by layer assembly and sputtering	Piezo-resistive	Strain	–	661.59($\sim 50\%$)	(Li <i>et al.</i> , 2020)
MoS ₂ xSe ₂ (1–x)	Cellulose paper	Vacuum filtration	Piezo-resistive	Pressure and strain	108.09 kPa ⁻¹ (~ 3.185 kPa)	27.57($\sim 36\%$)	(Bokka <i>et al.</i> , 2021)

– Not available.

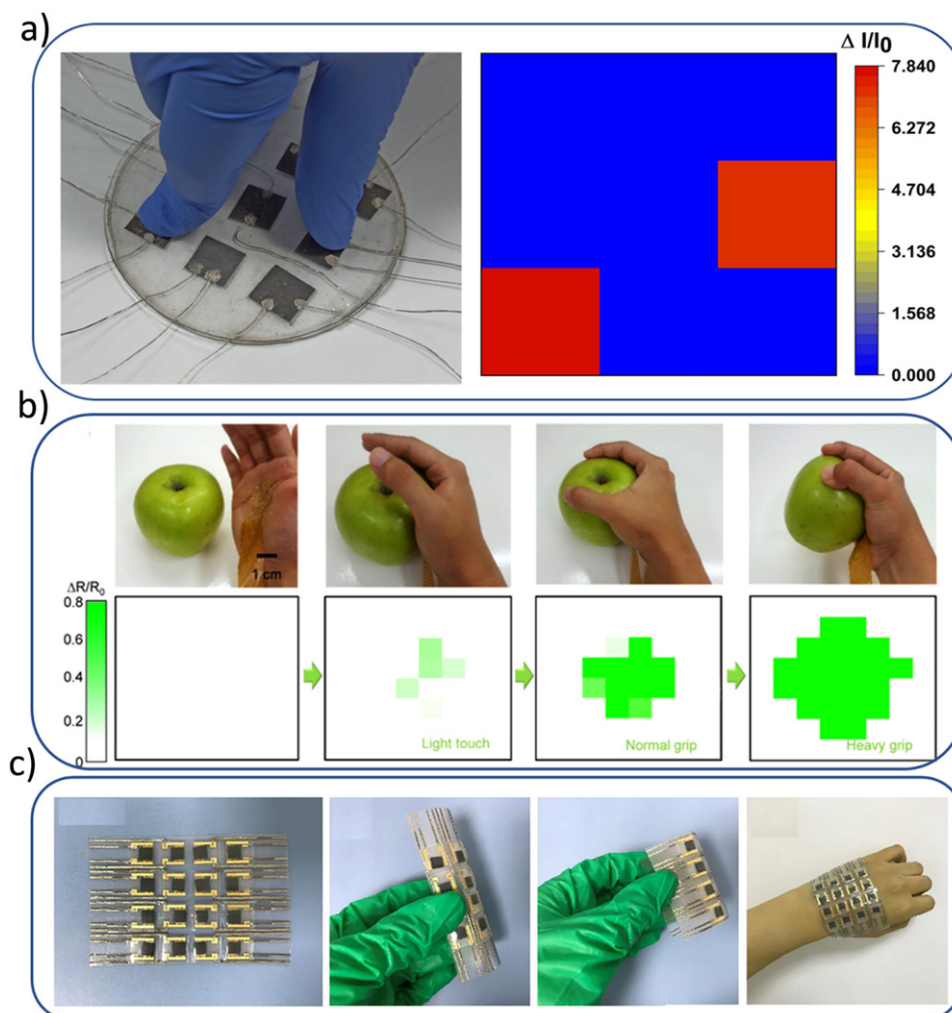


Fig. 11 (a) Digital image of the sensors array touched by two fingers and the corresponding pressure distribution map, (b) The active-matrix MoS_2 tactile sensor attached to the palm of a human hand, (c) Digital image of the pressure-based 4×4 array e-skin. Reproduced with permission Selamneni, V., Kunchur, A., Sahatiya, P., 2021b. Large-area, flexible SnS/paper-based piezoresistive pressure sensor for artificial electronic skin application. *IEEE Sens. J.* 21, 5143–5150, Copyright © 2021 IEEE. (b) Park, Y.J., Sharma, B.K., Shinde, S.M., *et al.*, 2019. All MoS_2 -based large area, skin-attachable active-matrix tactile sensor. *ACS Nano* 13, 3023–3030, Copyright 2019 American Chemical Society. Zheng, Y., Yin, R., Zhao, Y., *et al.*, 2021. Conductive MXene/cotton fabric based pressure sensor with both high sensitivity and wide sensing range for human motion detection and E-skin. *Chem. Eng. J.* 420, 127720, Copyright © 2020 Elsevier.

sensor was embedded within the crepe bandage to examine an ill patient's state of health. **Fig. 1(d)** illustrates the rise in temporal response for increasing knee bending angle, and current response of approximately $40\text{--}93\ \mu\text{A}$ for three bending angles was observed (Adepu *et al.*, 2022a). The ultrasensitive strain sensors can able to detect subtle changes in human motion.

For example, **Fig. 13(e)** depicts the strain sensor attached to the forehead, mouth, under the eyes, and neck to monitor the phonation and facial expressions (Wang *et al.*, 2017). The strain sensor was affixed on the wrist and elbow, and their current response was monitored, as shown in **Fig. 13(f)** (Selamneni *et al.*, 2021b). Recently, a new technology named transient electronics opposite, unlike conventional electronics, has been developed. The aim is to reduce the e-waste which is produced from various traditional electronics. **Fig. 13(g)** illustrates a water-soluble transient strain sensor attached to the neck to detect the movements of the neck (Bokka *et al.*, 2020). Also, the flexible strain sensor was used as an antenna for wireless human motion monitoring. **Fig. 1(h)** antenna sensor placed on palm to detect compressive bending and attached backhand to detect tensile bending. During the sensor test, it was noticed that there was a uniform variation in normalized frequency (Sindhu *et al.*, 2021).

Sports performance monitoring

In recent years, real-time sports monitoring has gained popularity due to the advancement in sensing technology. It provides quantitative information to understand the different body moments to improve training and prevent sports-related injuries. The body moments are captured by protractors, videography, IR cameras, accelerometers, etc. However, these methods are expensive,

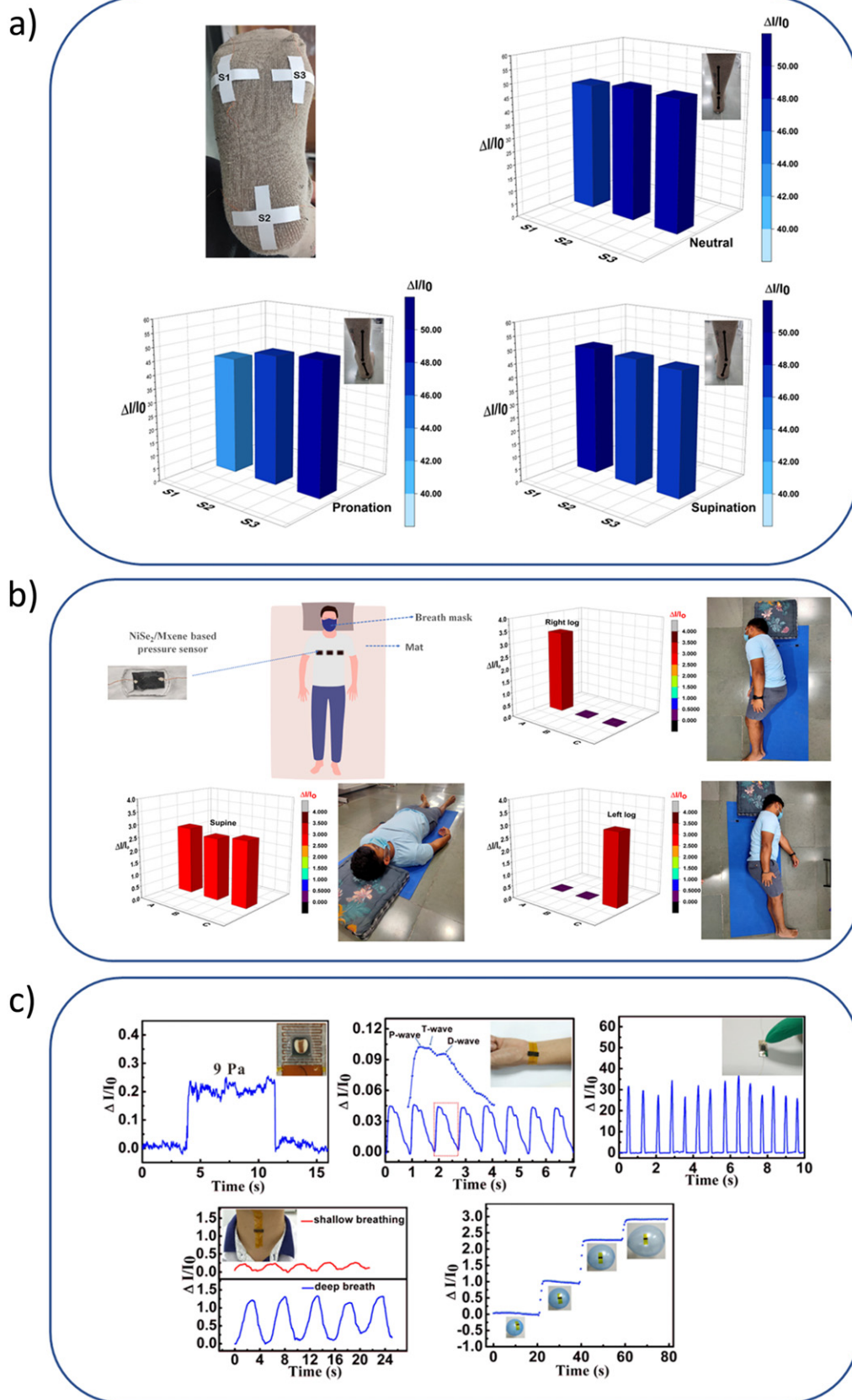


Fig. 12 (a) Fabricated pressure sensor integrated on foot and relative change in the device current for various gait. (b) Real-time observation of sleep monitoring using a flexible pressure sensor. (c) Real-time monitoring of physiological signals of the human body. Reproduced from (a) Kamath, K., Adepu,

V., Mattela, V., Sahatiya, P., 2021a. Development of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MoS}_2\text{Se}_{2(1-x)}$ nanohybrid multilayer structures for piezoresistive mechanical transduction. *ACS Appl. Electron. Mater.* 3, 4091–4104, Copyright © 2021 American Chemical Society (b) Adepu, V., Kamath, K., Mattela, V., Sahatiya, P., 2021a. Development of $\text{Ti}_3\text{C}_2\text{T}_x/\text{NiSe}_2$ nanohybrid-based large-area pressure sensors as a smart bed for unobtrusive sleep monitoring. *Adv. Mater. Interfaces* 8, 2100706, Copyright ©2021 John Wiley and Sons. (c) Yue, Y., Liu, N., Liu, W., *et al.*, 2018b. 3D hybrid porous MXene-sponge network and its application in piezoresistive sensor. *Nano Energy* 50, 79–87, Copyright © 2018 Elsevier.

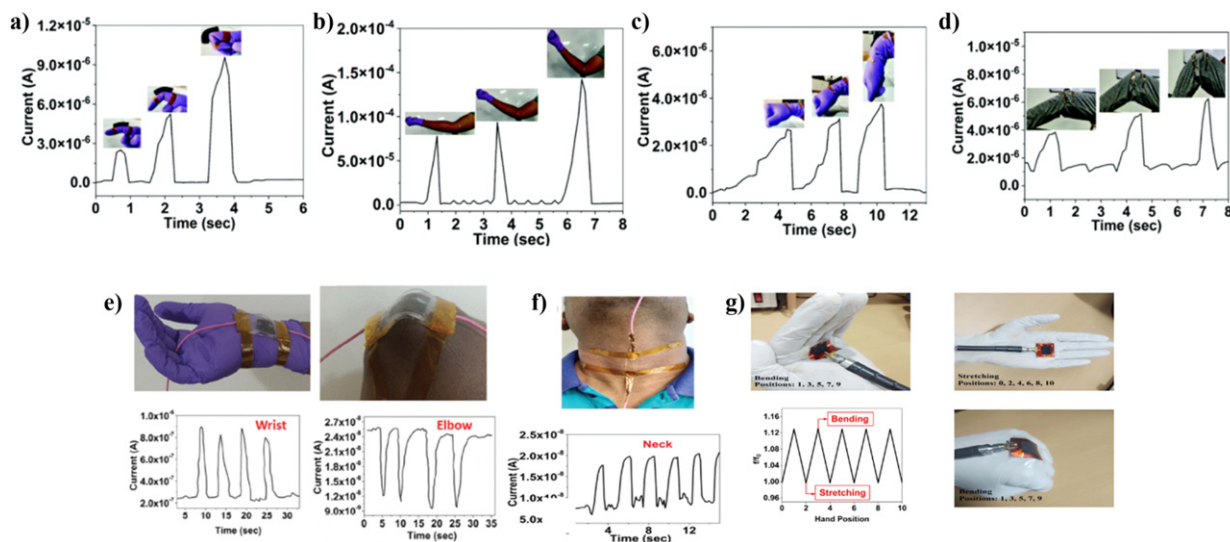


Fig. 13 The flexible strain sensor attached to a human body to sense various subtle movements (a) the finger joint, (b) elbow, (c) wrist (d) knee, (e) wrist, elbow (f) neck, (g) flexible strain sensor antenna. Reproduced with permission from (a–c) Adepu, V., Mattela, V., Sahatiya, P., 2021b. A remarkably ultra-sensitive large area matrix of MXene based multifunctional physical sensors (pressure, strain, and temperature) for mimicking human skin. *J. Mater. Chem. B* 9, 4523–4534, Copyright © 2021, Royal Society of Chemistry. (d) Adepu, V., Kamath, K., Siddhartha, S., Mattela, V., Sahatiya, P., 2022a. MXene/TMD nanohybrid for the development of smart electronic textiles based on physical electromechanical sensors. *Adv. Mater. Interfaces* 9, 2101687, Copyright ©2022 Wiley-VCH GmbH. (e–f) Bokka, N., Selamneni, V., Sahatiya, P., 2020. A water destructible SnS_2 QD/PVA film-based transient multifunctional sensor and machine learning assisted stimulus identification for non-invasive personal care diagnostics. *Mater. Adv.* 1, 2818–2830, Copyright ©2020, Royal Society of Chemistry. (g) Sindhu, B., Kothuru, A., Sahatiya, P., Goel, S., Nandi, S., 2021. Laser-induced graphene printed wearable flexible antenna-based strain sensor for wireless human motion monitoring. *IEEE Trans. Electron. Devices* 68, 3189–3194, Copyright ©2021, IEEE.

have inaccurate results, and restrict the body's moments (Li *et al.*, 2022). Flexible and wearable strain sensors accurately monitor real-time physiological signals from athletes. These sensors can attach to various body parts to track different body motions and provide physiological signals before, during, and after the activities (Souri *et al.*, 2020). Fig. 14(a) shows the fabricated wearable strain sensor using graphene fiber for tracking the basketball jump shot. The flexible strain sensors were attached to the player's elbow, shoulder, and wrist, and data were recorded. The flexible sensors successfully recorded the jump shot and responses from different joints, as shown in Fig. 14(a) (Zhang *et al.*, 2018). In another application, flexible sensors were fixed to the knee and monitored the running, jumping, walking, and squatting (Yamada *et al.*, 2011). Therefore, wearable strain sensors are advantageous for the continuous monitoring of health and wellness, human-friendly rehabilitation, and evaluating athletes sports performances.

Human-machine interface and gesture recognition

The primary objective of current technology is to create an intelligent human-machine interface, which can be accomplished through the wearable sensory system. Wearable strain sensors can be used to actuate smart robots via their signals. Fig. 14(b) illustrates the flexible strain sensor fabricated to be used for robotic arm control. The sensor sensing responses as a function of the degree of bend applied. The fabricated strain sensor is integrated into a smart glove system to remotely control the robotic arm (Gong *et al.*, 2015). Gesture identification and sensing have been a hot topic in human language technology (HLT) for interpreting real-time human gestures, which is especially important for deaf and hard-of-hearing people who can convey their basic needs through hand gestures. Fig. 14(c) shows the increase in temporal response for various applied strains and digital images of real-time hand gesture recognition. The strain sensors were affixed on the fingers, during hand gestures, the precise message matches to the appropriate finger move and sends to the smartphone via Bluetooth. These gestures could be used to communicate with those who are deaf, dumb, and physically challenged people (Veeralingam *et al.*, 2019). Also, The strain sensors are not limited to gesture recognition but are also used to study dynamic blood flow. Fig. 14(d) shows the digital image of a flexible PDMS tube that acts as an artery. The fabricated strain sensor was placed on the surface of the tube to detect the dynamic flow measurements inside the tube. Also, the strain sensor was able to detect the abnormal flow of blood (Kamath *et al.*, 2021).

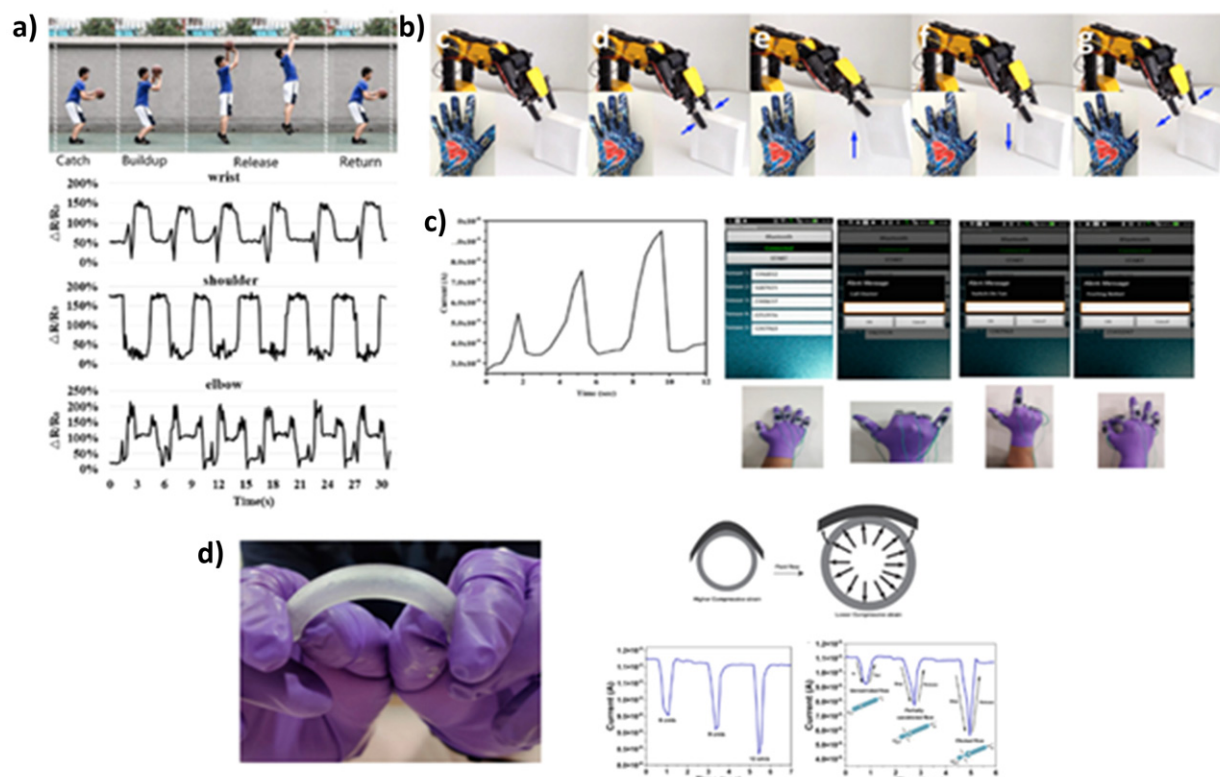


Fig. 14 (a) Flexible and wearable strain sensors for the sport performance analysis. (b) The remote controlling performance of four flexion sensors sewed on a textile glove. (c) Strain sensor temporal response and real-time gesture recognition and wireless display of popup. (d) The dynamic flow of the blood was studied using a flexible strain sensor. Reproduced with permission (a) Zhang, J., Cao, Y., Qiao, M., *et al.*, 2018. Human motion monitoring in sports using wearable graphene-coated fiber sensors. *Sens. Actuators A Phys.* 274, 132–140, Copyright ©2018, Elsevier. (b) Gong, S., Lai, D.T.H., Wang, Y., *et al.*, 2015. Tattoo-like polyaniline microparticle-doped gold nanowire patches as highly durable wearable sensors. *ACS Appl. Mater. Interfaces* 7, 19700–19708, Copyright ©2015, American Chemical Society. (c) Veeralingam, S., Sahatiya, P., Kadu, A., Mattela, V., Badhulika, S., 2019. Direct, one-step growth of NiSe_2 on cellulose paper: A low-cost, flexible, and wearable with smartphone enabled multifunctional sensing platform for customized noninvasive personal healthcare monitoring. *ACS Appl. Electron. Mater.* 1, 558–568, Copyright ©2019, American Chemical Society. (d) Kamath, K., Adepu, V., Mattela, V., Sahatiya, P., 2021a. Development of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MoS}_2\text{xSe}_{2(1-x)}$ nanohybrid multilayer structures for piezoresistive mechanical transduction. *ACS Appl. Electron. Mater.* 3, 4091–4104, Copyright ©2021, American Chemical Society.

Conclusion and Future Outlook

In summary, this review collective to its research advancement in flexible and wearable physical sensors, the preparation methods, the performance of the sensor, thorough underlying transduction mechanisms of various fabricated physical sensors, and typical applications of functional materials based on flexible sensors with different device structures has been discussed.

A surfeit of functional material based on flexible and wearable physical (pressure/strain) sensors developed recently with enhanced sensitivity has shown favorable potential in a wide range of applications. Despite the exhilarating progress, several challenges persist related to materials, sensing performance, and assimilation into wearable systems for continuous wireless monitoring in several practical applications.

In terms of functional materials, beyond understanding the properties of nanomaterials, the advancement of fabrication methods is necessary to attain cheaper, enhanced performance and reliable physical sensors. Also, organized analyses on the long-term biocompatibility of nanomaterials are in critical need to stimulate the real-time applications of nanomaterial-based flexible and wearable sensors, specifically in healthcare. Several functional materials have been utilized to develop different physical sensors and to confirm improved performance, additional attempts should be dedicated to augmenting the significant area growth with virtuous uniformity as well as developing the deficiency-free transport onto disparate substrates with raised quality and yield. Mountable assembly of nanomaterials with regulated density, minimal deficiency, excellent homogeneity, and superior longitudinal resolution must be additionally developed.

In terms of assimilating fabricated physical sensors into various wearable systems, one of the difficulties is the cross-sensitivity of numerous sensors. The fabricated sensor might respond to several other external stimuli applied, making it difficult to distinguish the particular kind of stimuli and intensity of each stimulus. A detailed study on the underlying transduction mechanism of the fabricated physical sensors with new nanomaterial-based hybrids needed to be studied to overcome the issues mentioned above. In particular, continuous accurate monitoring of the vital stats of human-related wireless monitoring is necessary, which needs further exploration for healthcare applications.

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Graphene-Based Electrochemical Sensors for Environmental Monitoring Applications

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Abstract

Graphene (Gr), a one-atomic thick layer of graphite arranged in a 2D hexagonal lattice, is being projected as the next-generation carbon material for vastly diversified sensing applications. Gr and its derivative, graphene oxide (GO) have unwrapped a new epoch in the expansion of electrochemical sensors because of their unique physico-chemical, electrical, mechanical properties and biocompatibility which hold extraordinary electrical and thermal conductivity, high electron mobility, good flexibility, wide electrochemical potential window, and high specific surface area. This article elaborates on the properties of Gr and GO and their applications in environmental monitoring as electrochemical sensors. In precise, we confer recent progressions of Gr/GO-based electrochemical sensors in important applications of environmental monitoring, highlighting the sensing performances which contain sensitivity, detection limit, selectivity, stability, reproducibility, and their validation in real samples. Fundamental sensing mechanisms have been scientifically discoursed to get a better perception of how Gr and GO contribute to the performance of each electrochemical sensor. Wherever appropriate, limits of the present methods and future viewpoint have also been sketched and conferred.

Key Points

- A compact knowledge on the properties, applications of graphene as electrochemical sensors for environmental monitoring.
- Essential sensing mechanism of graphene based electrochemical sensors is discoursed to get better insight.
- Analytical performances of various graphene and its composites based electrochemical sensors were categorically presented in tables and compared.
- Wherever relevant, limitations of current methodologies and future outlook have also been delineated.

Introduction

In recent times, with fast progress in industry and agricultural science, along with the great ingestion of several synthetic drugs in our daily life, the environment has been affected by numerous lethal pollutants, such as heavy metal ions, explosives, phenolic compounds, pesticides, gases, and so on. The presence of a very lesser amount of these toxic chemicals is hazardous, cancer-causing and directly comes into the food chain, which has threatened severely the environs together with the social health. Hence, it is essential to fabricate sensitive, low-priced sensors for rapid determination of these priority pollutants with high accuracy (Liu *et al.*, 2020; Buckley *et al.*, 2020; Rebelo *et al.*, 2021; Mois *et al.*, 2017). This has navigated the researchers to stress upon developing the sensors with high sensitivity, specificity, repeatability, low detection limit, and stability. A sensor is mainly an investigative device that quantitatively or semi-quantitatively transmutes the information about the existence of a physical (e.g. gas, temperature, light intensity) or chemical species (analyte) to a quantifiable signal. Its functioning involves two significant steps: (a) recognition and (b) transduction. In the course of recognition, the analyte interacts with the receptor molecules or the active sites involved in the structure of the recognition element of the sensor whereas the transducer decodes this occurrence into an appropriate signal like resistance, potential or current (Mois *et al.*, 2017; Sha *et al.*, 2017a, 2019; Sahatiya *et al.*, 2019). Numerous analytical methods like high-performance liquid chromatography, bienzymatic colorimetry, fluorescence spectroscopy, etc., have been developed for the detection of pollutants. These conventional methods are costly; include sophisticated equipment, the operational difficulty which makes them inappropriate for on-site monitoring. To overcome these problems, electrochemical sensors have engrossed substantial attention for the recognition of analytes because of their low-cost, straightforwardness, good sensitivity, continuous real-time sensing, and quick response (Dong *et al.*, 2021; Sivakumar and Lee, 2021; Sha and Bhattacharyya, 2020).

Of late, nanotechnology has unwrapped as one of the most motivating forefront fields. A widespread range of nano-materials of various structures, morphologies, chemical configurations with the essential surface properties, crystallographic coordination, and so on had navigated their use in the chemical sensing applications. In this aspect, Graphene (Gr), a one-atomic thick layer of graphite arranged in a two-dimensional (2D) hexagonal lattice has stimulated promptly increasing importance for potential applications in several fields like supercapacitors, methanol oxidation reactions, and sensing because of its extraordinary electrical conductivity of $\sim 1 \times 10^8 \text{ S m}^{-1}$, the thermal conductivity of $2000\text{--}4000 \text{ W m}^{-1} \text{ K}^{-1}$, the current density of $\sim 1.6 \times 10^9 \text{ A cm}^{-2}$, electron mobility of $2,00,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at an electron density of $\sim 2 \times 10^{11} \text{ cm}^{-2}$, the mechanical strength of 42 Nm^{-1} , the melting point of 4510 K , with good flexibility, transparency, wide electrochemical potential window (2.5 V in 0.1 mM phosphate-buffered saline) and

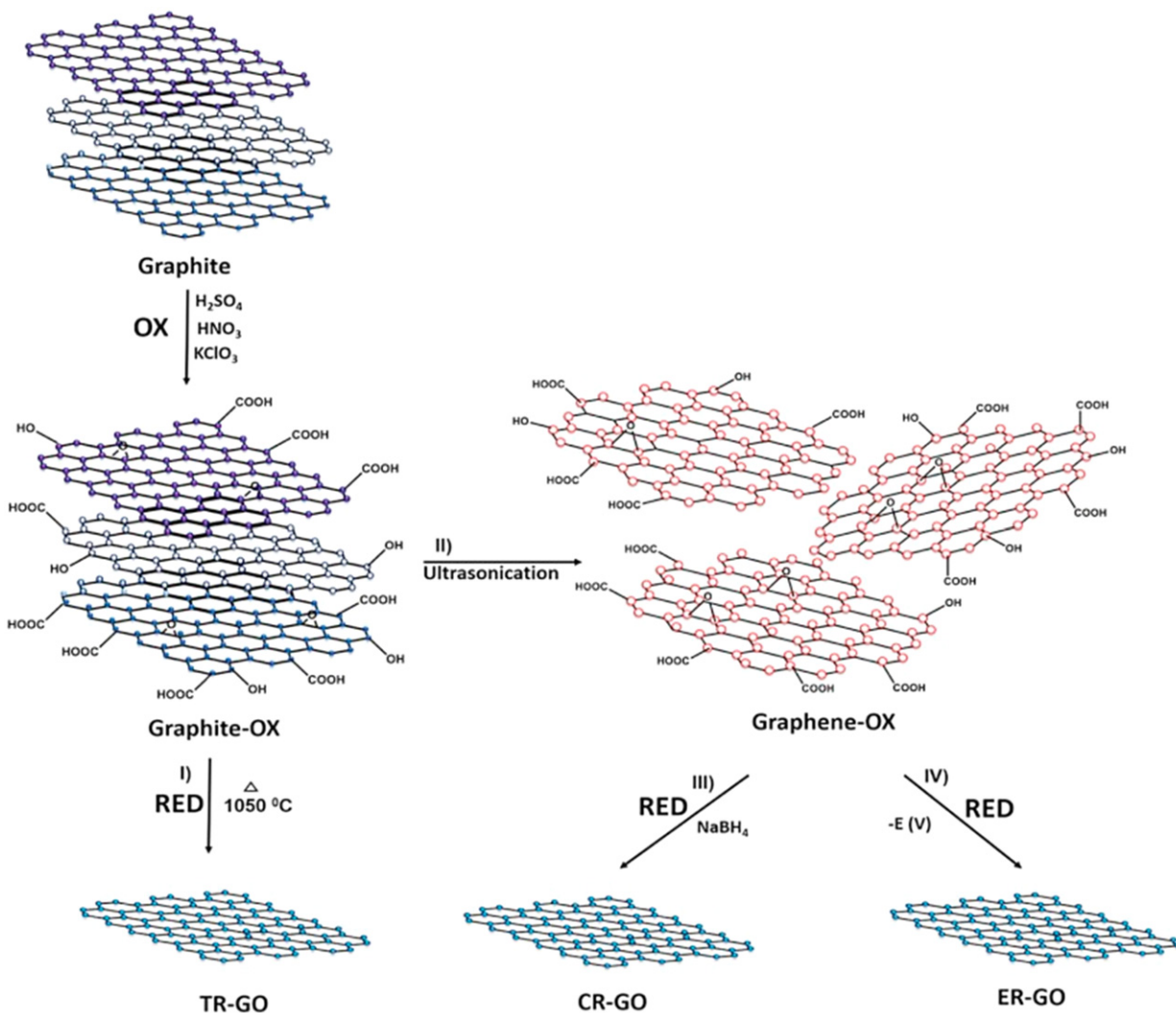


Fig. 1 Solution-based reduction techniques of GO. Republished with permission from Bahadır, E.B., Sezgentürk, M.K., 2016. Applications of graphene in electrochemical sensing and biosensing. *TrAC Trends in Analytical Chemistry* 76, pp.1–14.

high specific surface area (Sha and Badhulika, 2017, 2018a,b,c; Sha et al., 2017b). In Gr, each carbon atom shares with neighbors three in-plane σ -bonds and an out-of-plane π -bond (average interatomic distance = $1.42 \text{ \AA}$). One of the necessities for a classic electrochemical sensor is the good electro-catalytic ability of an electrode as this feature fundamentally increases the redox reaction. Incidentally, heterogeneous electron transfer and outstanding electrocatalytic properties of Gr make it a promising sensing material for electrochemical sensing applications. Nevertheless, Gr is a semi-metal with zero bandgap and is hydrophobic. These two features restrict its possibility in practical sensing applications. To enhance its properties and magnify the scope of applications, a Gr derivative, graphene oxide (GO), has been developed extensively. GO is a Gr sheet decorated with oxygen holding functional groups (e.g., carbonyl, carboxyl, hydroxyl, and epoxy groups) on the both sides of basal plane and edges and attained by oxidation of graphite using the familiar Hummers method. The presence of these hydroxyl and epoxy groups delivers surface functionalization with the anticipated biomolecules and brilliant aqueous dispersibility. Unlike Gr, in GO, bandgap can be introduced because of quantum-confinement and chemically, thermally, or electrochemically regulated by controlling layers, shape, distribution, size, composition, and relative fraction of sp^3 hybridized domains of GO. Besides, numerous other characteristics including low fabrication cost, extraordinary surface area, decent durability, and biocompatibility offer GO a dominant platform for electrochemical sensing applications (Sha et al., 2017a; Rabchinskii et al., 2021; Bahadır and Sezgentürk, 2016).

Until now, numerous approaches such as solution-based reduction of GO, chemical vapor deposition (CVD), plasma-enhanced CVD (PE-CVD), hydrothermal, exfoliation and cleavage of natural graphite, electric arc discharge, micromechanical exfoliation of graphite, epitaxial growth on electrically insulating surfaces, like SiC, and opening CNTs, etc., have been developed towards the synthesis of Gr. For instance, GO can be reduced in several ways like thermally (TR), chemically (CR), electrochemically (ER) as depicted in Fig. 1. Each synthesis method has its advantages and intrinsic limitations. Epitaxial growth of Gr on SiC requires very high temperature whereas the mechanical exfoliation route is not suitable for bulk production as it provides low-

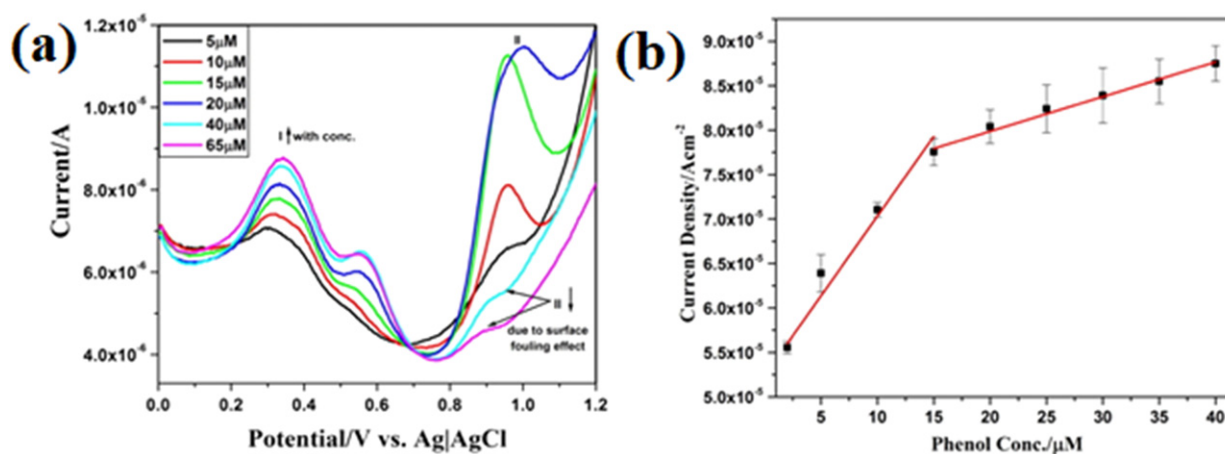


Fig. 2 (a) DPV plots of the rGO-ZnO composite based sensor at different concentrations of phenol in 0.1 M H_2SO_4 electrolytic solution; (b) Calibration curve representing the response of electrodes towards phenol. Republished with permission from Sha, R., Puttapati, S.K., Srikanth, V. V., Badhulika, S., 2017c. Ultra-sensitive phenol sensor based on overcoming surface fouling of reduced graphene oxide-zinc oxide composite electrode. *Journal of Electroanalytical Chemistry* 785, 26–32.

quality Gr. CVD is an efficient approach for practical applications as it provides high-quality Gr (Sha *et al.*, 2017a; Bahadır and Sezgentürk, 2016; Wei and Liu, 2010).

This book chapter describes the properties of Gr, and their applications in sensors for environmental monitoring. Essential sensing mechanisms are thoroughly discoursed to deliver a better understanding of how Gr is attributed in each sensor. Moreover, a summary of recent progress of Gr-based nanostructures in the field of electrochemical sensors is made, highlighting their sensing performances which consist of sensitivity, selectivity, detection limit, reproducibility, stability, repeatability, and their applications in real environs. Lastly, wherever relevant, boundaries of existing approaches and future viewpoints have also been delineated.

Environmental Monitoring Applications

Sensing of Phenolic Compounds

The environmental pollution caused by poisonous, organic molecules like phenol and phenolic compounds has gained wide importance in both the academic circles and research groups due to their negating effects on humans. Phenol and phenolic compounds, for instance, 4-aminophenol (4-AP), 4-chlorophenol (4-CP), 2-chlorophenol (2-CP), bisphenol A (BPA), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP), etc., are recognized through either oxidation or reduction at the electrode surface. Identifying these molecules as ecological estrogens is significant owing to their harmful effects (Baig *et al.*, 2021). Sha *et al.* (2017c) reported an ultra-sensitive non-enzymatic phenol sensor based on the reduced graphene oxide (rGO)-zinc oxide (ZnO) composite electrode wherein this composite was prepared via a wet chemical process. The phenol sensing was examined by differential pulse voltammetry (DPV) which generated two peaks at 0.35 V (peak I) and 0.94 V (peak II) as presented in Fig. 2. (a). The current of anodic peak II increased only at lower concentrations of phenol (up to 20 μM) and started falling at higher phenol concentrations due to surface fouling effect. Phenoxyl radicals were further oxidized to Hydroquinone which would be adsorbed on the electrode surface. Hence, no further oxidation of phenol was possible. Phenol recognition was done at a lower potential (0.35 V) as it eradicates the need for surface renewal of the electrode before each scan caused due to surface fouling thus facilitating stable and reproducible detection. This sensor responded linearly to phenol over two ranges, one in the range 2–15 μM with an ultrahigh sensitivity of $1.79 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ and the other in the range 15–40 μM with a sensitivity of $0.389 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ (Fig. 2. (b)) with good durability of 3 days, selectivity over ethanol, 2-CP and a low detection limit of 1.94 μM . The sensing ability was studied in terms of forward-biased nano-Schottky barriers at the composite electrode interface. Further, the applicability of this composite base sensor was validated through the detection of phenol contents in potable drinking water with the recovery% of 98%–109.2%.

Arfin and Rangari (2018) described the ZnO functionalized GO-based electrochemical sensor for detection of phenol where this composite was prepared at a weight ratio of GO and ZnO = 1:1. Phenol was detected in the electrolytic solution of pH 7 via direct oxidation at the surface of the composite-based electrode and also showed better performance than only GO. The composite-based electrochemical sensor displayed good linearity, the low detection limit of 2.2 nM over the phenol concentrations range of 5–155 μM with good repeatability, stability of 30 days and selectivity over other phenolic compounds and ions. But the applicability of this sensor in real samples such as water bodies was not checked. Singh *et al.* (2016) developed the sensing of phenol using electrochemically reduced GO (E-rGO) where the GO was reduced electrochemically on the surface of the electrode. The electrochemical impedance spectroscopy (EIS) was used for the recognition of phenol in the phosphate buffer of pH 7 over the concentration range of 1–40 μM . With the increasing concentrations of phenol, the diameter of the semi-circle decreased as well as the double-layer

capacitance increased. This sensor exhibited good selectivity over benzene, cresol, nitro-phenol, resorcinol and toluene with good sensitivity of $-7.6 \Omega \text{ cm}^{-2} \mu\text{M}^{-1}$ with a detection limit of $0.2 \mu\text{M}$. This sensor was also validated through the determination of phenol in the water samples, collected from four different villages. This result ensured its applicability in real environments. [Nurdin et al. \(2019\)](#) demonstrated the Gr-TiO₂-carbon paste composites for the phenol sensing in $0.1 \text{ M H}_2\text{SO}_4$ electrolytic solution where phenol was detected by direct oxidation at the surface of the composite based electrode at a low potential of 0.12 V . This sensor displayed a very low detection limit of $3.66 \times 10^{-5} \mu\text{M}$ with brilliant stability and reproducibility over the concentration range of $1 \mu\text{M}$ – 0.1 M of phenol. This excellent sensing performance was due to high conductivity resulting from Gr and the large electro-active surface area of the composite for direct electron transfer throughout the redox reactions. However, validations in real samples as well as selectivity of this sensor over other phenolic compounds were not tested. [Zhou et al. \(2013\)](#) presented the rGO based biosensor for sensing of phenols in air-saturated HAC–NaAC buffer solution of pH 4.5 where an enzyme, namely laccase (Lac) from *Rhus vernificera* was covalently immobilized on the surface of 1-aminopyrene (1-AP) functionalized rGO based electrode by encapsulation with chitosan (Chit). Phenols were detected through oxidation at the surface of the Lac/AP-rGO/Chit based electrode by the redox reaction of the T1 site of Lac, where the electron was transported into the electrode through the direct electron transfer procedure between Lac and the electrode surface. The sensitivities of this bioelectrode were 14.16 and $15.79 \mu\text{A mM}^{-1}$ over the linear ranges of 3 – 2000 , 15 – $700 \mu\text{M}$ for hydroquinone and catechol, respectively with a detection limit of 2 and $7 \mu\text{M}$, good repeatability, stability of 7 days, selectivity over ions and other organic molecules. Further, this biosensor was validated through successful sensing of hydroquinone in tap water, lake water samples with decent recovery% of $82.7\% \pm 10$ – $105.9\% \pm 8\%$, thus, endorsing the potential application to measure phenols in real environments. [Pan et al. \(2015\)](#) reported the 4-nonyl-phenol (NP) sensor using the molecularly imprinted polymer (MIP), N-doped Gr nanoribbons (NGNRs) and ionic liquid (IL) where the NGNRs were synthesized through opening multi-walled carbon nanotubes, followed by hydrothermal treatment with ammonium–NaOH solution. The MIP was prepared by electro-polymerization with the optimal potential scan cycle number of 9 at the NGNRs-IL composite film based electrode, with NP as a template, o-phenylenediamine and o-toluidine as copolymerization monomers. This optimal sensor showed a sensitivity of $3.4 \mu\text{A} \mu\text{M}^{-1}$, a low limit of detection of 8 nM over the NP concentration range of 0.04 – $6 \mu\text{M}$ with good reproducibility, stability of 1 month and excellent selectivity. These good performances were attributable to good dispersibility and higher conductivity of NGNRs. Here, the MIP enhanced the selectivity of the sensor. Further, the practical viability of the sensor was assessed by detection NP in lake water, river water and tap water with an acceptable recovery% of 93.5% – 103.5% . [Gan et al. \(2016\)](#) described the GO-wrapped carbon sphere (CS)–Ag spheres composite based electrochemical sensor for recognitions of chlorinated phenols where a template-activated scheme was employed to prepare core/shell structured CS–Ag spheres composite based on one-pot hydrothermal treatment. 2-CP, 4-CP, 2,4-DCP and 2,4,6-TCP were sensed at the surface of the composite based electrodes via oxidation with low detection limit, good reproducibility, selectivity and stability. These good performances were ascribed to enlarged surface area and catalytic activity of the composite originating from the 3D interconnected structure with a closely integrated interface, quick electron transfer kinetics, and high electrical conductivity resulting from the presence of Ag nanostructures without any agglomeration. Moreover, the practicability of this sensor was examined by the determination of chlorinated phenols in river water, lake water and tap water samples with a decent recovery% of 92% – 116% . [Li et al. \(2019\)](#) developed the Gr nanoplatelet supported CeO₂ composites for electro-catalytic oxidation of multiple phenolic compounds like tetra-bromo-bisphenol A (TBBPA), catechol, diethylstilbestrol (DES), and NP in 0.1 M pH 6 phosphate buffer solutions where the CeO₂ nanocubes, nanopolyhedras, and nanorods were prepared via a hydrothermal way. These CeO₂ nanomaterials were then loaded on the support of Gr nanoplatelets to obtain the Gr-CeO₂ composites. These sensors exhibited good sensitivity, low detection limit with good selectivity over other common phenols. But stability of these sensors was not investigated. But, validation was done through sensing of TBBPA, catechol, DES and NP in lake water samples with good recovery%. [Zheng et al. \(2019\)](#) demonstrated the polyaniline-porous polyacrylonitrile-Gr composite based biosensor for recognition of p-cresol in 0.02 M phosphate buffer solution of pH 6 where the enzyme, viz. polyphenol oxidase was immobilized in the surface of this composite modified electrode. This bioelectrode revealed a high sensitivity of $6.46 \mu\text{A} \mu\text{M}^{-1} \text{ cm}^{-2}$, good stability, reproducibility, selectivity over metal ions, glucose, ascorbic acid, etc., with a low detection limit of $0.26 \mu\text{M}$. Porous polyacrylonitrile was utilized as electron transfer shuttle in a redox mediator and offered as a satisfactory microenvironment for adsorbing enzyme, thus, circumventing the currents drifting whereas Gr and conducting polymer, polyaniline improved the overall conductivity of the sensor. The applicability of this electrode was inspected by recognition of p-cresol in the water samples with the decent recovery% of 102% – 106.7% . [Gan et al. \(2017\)](#) fabricated the flexible GO wrapped SnO₂ hollow spheres composite based electrochemical sensor for simultaneous detection of 4-AP and 4-CP wherein this composite was prepared by the hydrothermal route. An oxidation reaction containing two electrons and protons facilitated the electrochemical sensing of 4-AP while the oxidation reaction of 4-CP was a one electron and one proton process at the surface of the composite electrode. This composite based sensor showed a good sensitivity with good reproducibility, stability of 20 days and selectivity over metal ions as well as other phenolic compounds. This good electrochemical sensing performance was ascribed to the catalytic activity of the composite and the high accumulation capacity of the SnO₂ nanowalls. The ability of this sensor for real-time applications was verified via sensing of 4-AP and 4-CP in river water, lake water, pond water and spring water samples with a decent recovery% of 92.3% – 108% . [Rahman et al. \(2018\)](#) reported the polyaniline-Gr-carbon nanotubes composite based electrode for sensing of 4-AP by I–V method where the composite was synthesized via in-situ polymerization route. The optimal sensor revealed a high sensitivity of $2.1873 \mu\text{A} \mu\text{M}^{-1} \text{ cm}^{-2}$ and detection limit of 63.4 pM over the linear dynamic range of 0.1 nM – 0.01 M of 4-AP with good reproducibility, stability of 7 days and selectivity over benzaldehyde, dichloromethane, acetone, chloroform, ethanol, pyridine, n-hexane. The validity of this sensor was also examined via sensing of 4-AP in tap water, seawater, PC-bottle water, food packaging-bag water and industrial effluents.

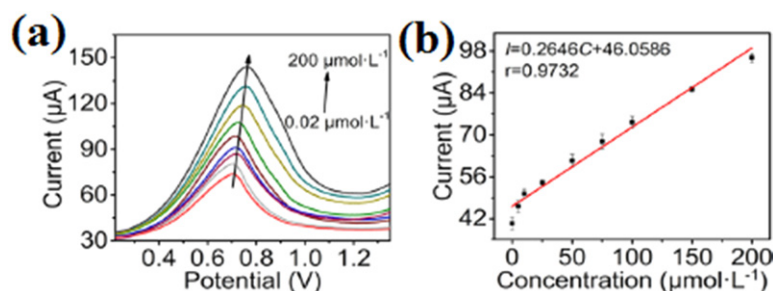


Fig. 3 (a) DPV plots of the NiS_2 micro blocks- MoS_2 nanosheets-rGO composite based sensor at different concentrations of BPA in a buffer solution of pH 7; (b) Calibration curve representing the response of electrodes towards BPA. Republished with permission from Yuan, J., Jiang, L., Che, J., He, G., Chen, H., 2021. Composites of NiS_2 microblocks, MoS_2 nanosheets, and reduced graphene oxide for energy storage and electrochemical detection of bisphenol A. *ACS Applied Nano Materials* 4 (6).

Bisphenol A (BPA) is an endocrine-disrupting compound that can imitate estrogen and result in adverse health effects on animals as well as humans. The widespread use of BPA-based polymers has directed ecological pollution. As an estrogen imitator, BPA makes a hormonal reaction even at a very low concentration, thus stimulating discrepancy in the endocrine system. Hence, monitoring of BPA is of prime significance for the protection of human health and the environment (Reza *et al.*, 2015; Niu *et al.*, 2013). Bas *et al.* (2021) presented the metal ferrites (MFe_2O_4 , M: Ni, Cu, Zn) – rGO composite based electrochemical sensor for detection of BPA where these composites were synthesized by a hydrothermal technique. The NiFe_2O_4 -rGO based electrode displayed a better sensing performance towards the oxidation of BPA than the CuFe_2O_4 , ZnFe_2O_4 -based electrodes with a sensitivity of $0.6132 \mu\text{A} \mu\text{M}^{-1}$, good reproducibility, repeatability, stability of 14 days and selectivity over phenol, other organic compounds and metal ions. This superior sensing performance of the NiFe_2O_4 -rGO based electrode as compared to others was due to its better conductivity and greater surface area. Furthermore, validation was done via detection of BPA in the water bottle samples with the recovery% of 102.15%–102.87%. Wang *et al.* (2021) reported an electrochemical BPA sensor using the Au nanoparticles- MoS_2 nanoflowers-IL-functionalized Gr composite. This sensor exhibited a detection limit of $0.028 \mu\text{M}$, acceptable sensitivities over two regions with decent stability of 1 week, good selectivity over metal ions and organic molecules. This good electrochemical sensing performance of the Au nanoparticles- MoS_2 nanoflowers-IL-functionalized Gr composite based sensor was attributed to (1) huge specific surface area and numerous active sites of the MoS_2 , (2) improved the electro-catalytic properties originating from the Au nanoparticles and (3) great ionic conductivity, good solubility, and excellent electrical conductivity resulting from the presence of Gr. But, linearity in this sensor was not good. This electrochemical sensor was also used toward the recognition of BPA in lake water samples with the acceptable recoveries of 95.7%–105.4%. Beduk *et al.* (2020) described a mask-free, MIP sensor based on laser scribed Gr for BPA recognition. The CO_2 laser was employed for the fabrication of laser scribed Gr electrodes with extraordinary conductivity and multilayered structure via less laser speed/power of $2.8 \text{ cm s}^{-1}/3.2 \text{ W}$ and low resistivity $58 \Omega/\text{square}$ on flexible polyimide sheet leading to the great active surface area of the sensor. It was further functionalized with imprinted polypyrrole with a known amount of BPA as a template molecule. This MIP-based sensor was reused five times via washing it with acetic acid/ methanol (3:7) solvent mixture to take BPA out from the earlier made cavities. This sensor displayed a good sensitivity, stability of 20 days with selectivity over estradiol, epinephrine, dibutyl phthalate, gallic acid, caffeic acid, 4-chlorophenol and Bisphenol F. This sensor was effectively used for the sensing of BPA in tap, mineral water and in plastic samples with the satisfactory recoveries of 88%–110%. Yuan *et al.* (2021) developed the NiS_2 microblocks- MoS_2 nanosheets-rGO composite for electrochemical sensing of BPA where this composite was prepared by a two-step hydrothermal route. The BPA sensing was tested by DPV which generated one oxidation peak at 0.7 V as presented in Fig. 3. (a) over the concentrations range of 0.02–200 μM with a sensitivity of $0.265 \mu\text{A} \mu\text{M}^{-1}$. Fig. 3. (b) displays the corresponding calibration curve. The good electrochemical sensing performance of this electrode was ascribed to (a) an enlarged number of active sites in composite originating from NiS_2 micro blocks and MoS_2 nanosheets wrapped by rGO layers; (b) improved permeability of electrolytic ions and the adsorption of BPA molecules resulting from 2D MoS_2 and rGO layers with huge specific surface area, and (c) good electrical conductivity of rGO and structural stability of MoS_2 . But the selectivity, stability and applicability of this sensor were not evaluated.

Alam and Deen (2020) demonstrated an electrochemical BPA sensor based on the GO- β -cyclodextrin-functionalized multi-walled carbon nanotubes composite where the covalent attachment of multi-walled carbon nanotubes with β -cyclodextrin was accomplished by a one-step Steglich esterification reaction. A diffusion-controlled oxidation reaction containing equal numbers of protons and electrons enabled the electrochemical sensing of BPA. This sensor displayed a two-step linear response from 0.05 to 5 μM and 5–30 μM and a limit of detection of 6 nM with good reproducibility, stability of 4 weeks and selectivity over common metal ions, ascorbic acid, dopamine, and acetaminophen. This excellent performance of the composite-based sensor was due to the high surface area of GO and carbon nanotubes, and the greater host – guest interaction ability of β -cyclodextrin. Its practical application was further confirmed by detecting the concentration of BPA in tap, bottled, and lake water samples with recovery% of 96%–104.8%.

Detection of Heavy Metal Ions

Some heavy metal ions like iron, manganese, and zinc in small amounts are nutritionally indispensable for a healthy life. Nevertheless, certain heavy metal ions display a tendency to bind with ligands of biomolecules containing N, S, and O. So, even

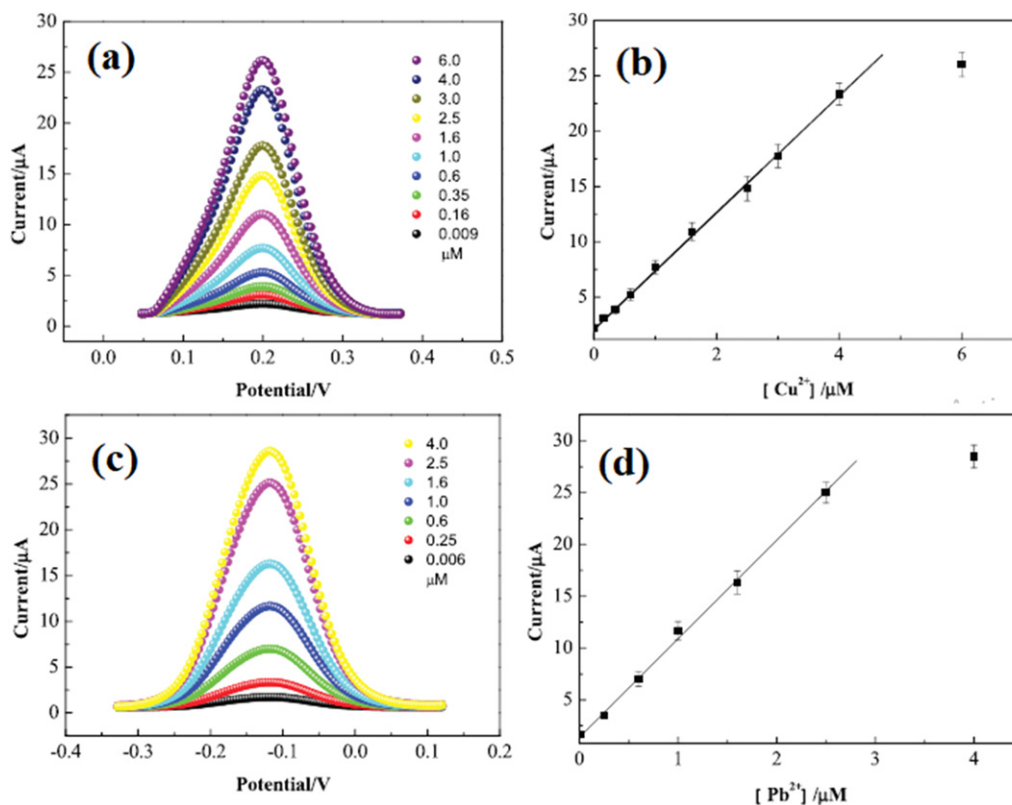


Fig. 4 (a) OSWVs of the Gr nanodots-encaged porous gold electrode for recognition of Cu^{2+} in ammonium acetate solution of pH = 5; (b) Calibration curve representing the response of electrodes towards Cu^{2+} ; (c) OSWVs of the Gr nanodots-encaged porous gold electrode for recognition of Pb^{2+} in ammonium acetate solution of pH = 5; (d) Calibration curve representing the response of electrodes towards Pb^{2+} . Reprinted with permission from Zhu, H., Xu, Y., Liu, A., *et al.*, 2015. Graphene nanodots-encaged porous gold electrode fabricated via ion beam sputtering deposition for electrochemical analysis of heavy metal ions. *Sensors and Actuators B: Chemical* 206, 592–600.

little concentrations of these heavy metal ions can cause severe health complications including those affecting the central nervous system (Hg^{2+} , Pb^{2+} , As^{3+}); the kidneys or liver (Cu^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+}); or skin, bones, or teeth (Ni^{2+} , Cu^{2+} , Cd^{2+} , Cr^{2+}). Moreover, the pollution triggered by poisonous heavy metal ions has attracted wide consideration globally. Even though these can gradually accumulate by the food chain, they are excreted. Hence, it is essential to design high-performance sensors for the recognition of heavy metal ions for the protection of human health and the environment (Karthik and Thambidurai, 2017; Thiruppathi *et al.*, 2017). Theeazen *et al.* (2021) reported the rGO-based electrochemical sensor for the recognition of Cd^{2+} and Pb^{2+} where an optimization study of the reduction of GO was performed by varying the numbers of voltammetric cycles like 3, 6, 9, and 12. The rGO based electrode with six voltammetric cycles (rGO-6) displayed the best performance among all rGOs. In presence of bismuth, this optimal electrode showed high sensitivities, low detection limits, good repeatability and stability. Even if this work utilized a green approach to prepare the sensing material, selectivity and validation of this sensor in real samples were not assessed. Akhtar *et al.* (2020) described the polyaniline-alanine-rGO composite based electrochemical sensor for the detection of Cd^{2+} , Pb^{2+} , and Cu^{2+} where this composite was prepared via an in-situ oxidative polymerization route. This sensor revealed good sensitivity, low detection of limit, with decent reproducibility and selectivity over other inorganic ions and nitrobenzene. This good sensing performance was ascribed to the presence of the functional groups like $-\text{C}=\text{O}$, $-\text{NH}_2$, $-\text{OH}$, and $-\text{COO}-$ of alanine and polyaniline coupled with rGO and the larger electro-active surface area of the composite (0.19 cm^2) than only rGO (0.16 cm^2) and only polyaniline (0.10 cm^2). The efficacy of this sensor towards sensing traces of Cd^{2+} , Pb^{2+} , and Cu^{2+} in tap water was also checked. Cheng *et al.* (2019) developed the rGO - silver nanoparticles based composite for sensing of Cu^{2+} , Cd^{2+} , and Hg^{2+} . The pristine GO was functionalized with triethylene-tetramine (TETA), and the composite was synthesized using TETA as the reductant through a hydrothermal technique. Although these sensors showed low detection limits towards sensing of Cu^{2+} , Cd^{2+} , and Hg^{2+} over the concentrations ranging from 10^{-9} to 10^{-5} M , their selectivity, reproducibility, stability and validation in real samples were not inspected. Zhu *et al.* (2015) developed the Gr nanodots-encaged porous gold electrode for recognition of Cu^{2+} and Pb^{2+} where the composite was prepared by the ion beam sputtering deposition technique. An optimization study was performed to check the impact of the thickness of the composite based electrode. The peak current started falling beyond the thickness of 40 nm. Fig. 4. (a) depicts the osteryoung square wave voltammetry (OSWV) plots for recognition of Cu^{2+} whereas Fig. 4. (b) displays corresponding calibration curve representing the response of electrodes towards Cu^{2+} . Cu^{2+} ions were sensed via electro-oxidation at the surface of the composite based electrode over the concentration range of 0.009–4 μM. Fig. 4. (c)

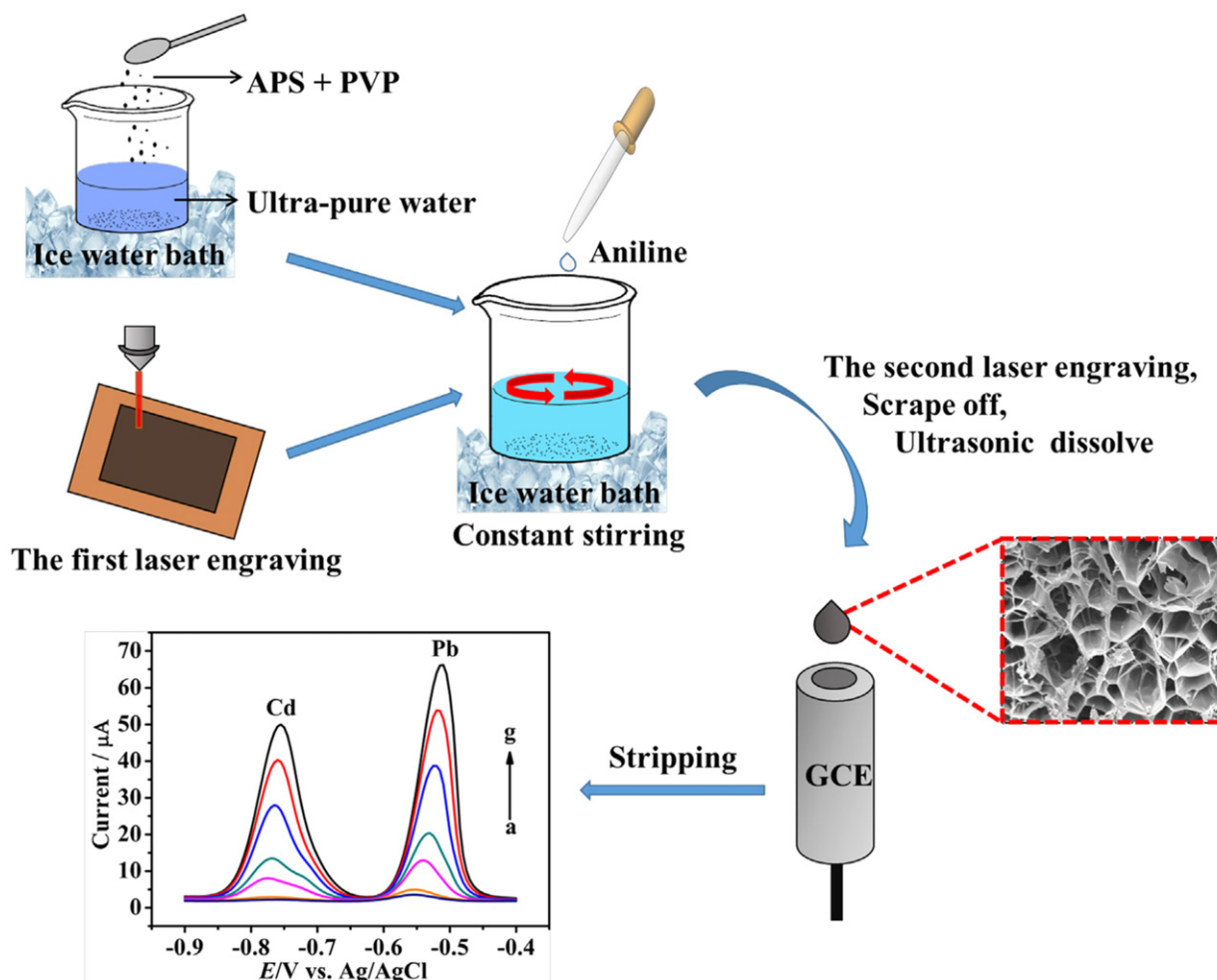


Fig. 5 Diagram of the fabrication method of the N@LEG based electrochemical sensor for simultaneous detection of Cd²⁺ and Pb²⁺. Reprinted with permission from Lin, X., Lu, Z., Dai, W., *et al.*, 2018. Laser engraved nitrogen-doped graphene sensor for the simultaneous determination of Cd (II) and Pb (II). *Journal of Electroanalytical Chemistry* 828, 41–49.

represents the OSWV plots for recognition of Pb²⁺ whereas Fig. 4. (d) illustrates corresponding the calibration curve representing the response of electrodes towards Pb²⁺. Pb²⁺ ions were sensed via electro-oxidation at the surface of the composite based electrode over the concentration range of 0.006–2.5 μM. This sensor exhibited good selectivity over other heavy metal ions, linearity and stability of 40 days. This high performance was attributed to the large electro-active surface area originating from the 3D structure of the composite which allows more metal ions to react with the electrode. But, validation in real samples and detection limits of this sensor were not estimated. Cui *et al.* (2018) fabricated the thiazole (T) derivatives functionalized Gr decorated with F, Cl and I-SnO₂ nanoparticles composite based electrochemical sensors for recognition of Cu²⁺ individually and then simultaneously determination of Cd²⁺, Cu²⁺ and Hg²⁺. These composites were synthesized by a hydrothermal route. But, the F-SnO₂/T/rGO composite based electrochemical sensor revealed better performance in 0.1 M phosphate buffer solution of pH 4.5 than others due to the unique properties of fluoride anions. This sensor exhibited a high sensitivity of 0.014 μA nM⁻¹ and a detection limit of 0.3 nM over the Cu²⁺ concentration range of 2–1000 nM. Further, the F-SnO₂/T/rGO composite based electrochemical sensor was employed to sense Cd²⁺, Cu²⁺, Hg²⁺ at different redox potentials (–0.8 V, –0.1 V and 0.3 V respectively) simultaneously in 0.1 M phosphate buffer solution of pH 4.5 over the linear dynamic range of 20–2000 nM with good selectivity, stability of 2 weeks. Its practicality was assessed by detection of Cd²⁺, Cu²⁺, Hg²⁺ in lake water samples with recovery % of 90%–106.0%. The combination of soft organic molecules and hard nanoparticles delivered more adsorption sites and some distinctive microstructure between Gr sheets which were favorable for the transportation of metal ions and electrons.

Lin *et al.* (2018) presented the N-doped laser engraved Gr (N@LEG) based electrochemical sensor for the simultaneous recognition of Cd²⁺ and Pb²⁺ where the N@LEG was prepared by introducing polyaniline and polyvinylpyrrolidone as N-dopant (Fig. 5). The optimal sensor showed the detection limits of 1.08 g L⁻¹ for Cd²⁺ and 0.16 g L⁻¹ for Pb²⁺ with notable sensitivity, selectivity over other heavy metal ions, reproducibility and stability of 2 weeks.

Detection of Explosives

The augmented concern for homeland safety has steered to a rise in research into an extensive range of schemes capable of sensing explosive nitroaromatic compounds (NACs) for example nitrobenzene, 2-nitrotoluene (2-NT), p-nitrophenol (p-NP), 4-nitrotoluene (4-NT), d 2,4,6-trinitroanisole (TNA), 2, 4-dinitrotoluene (DNT) and 2, 4, 6- trinitrotoluene (TNT), etc., at mostly trace levels which are also able to affect human health (Chen *et al.*, 2011; Caygill *et al.*, 2013). Niu *et al.* (2021) reported the si-doped Gr nanosheets as a metal-free catalyst for electrochemical recognition of TNT by reduction of nitro groups to amino groups where this composite was prepared by high-temperature annealing of GO and tetraethoxysilane mixture in a sealed glass ampoule. This sensor also showed a detection limit of 1.2 ppb towards TNT sensing. Moreover, nitrobenzene, 2-NT, 4-NT, and DNT had been electrochemically reduced on the composite electrode surface. Nitro groups were activated through the hydrogen bonding process, which was between oxygen atom in nitro group and hydrogen atom in hydroxyl group on si-doped Gr nanosheets. These activated nitro groups were effortlessly reduced to amino groups through $6e^-/6H^+$ process. Both the outstanding electrical conductivity and the rich surface hydroxyl groups stimulated the electrochemical sensing capability of the composite to nitroaromatic compounds. But, the selectivity, stability, reproducibility, applicability of this sensor were not assessed. Zhang *et al.* (2018) described the metal-free, base washed N- and S-codoped graphene nanoribbons (BW-NS-rGONRs) based electrochemical sensor for detecting of TNT via reduction where a substantial amount of carbonaceous oxidative debris resided in graphene oxide nanoribbons (GONRs) was created from unzipping the multiwalled carbon nanotubes. The adsorbed oxidative debris was removed via base washing. This sensor displayed a high sensitivity, a low detection limit of 0.1 ppb over the concentrations range of 0.0008–5.1 ppm TNT and good selectivity over nitrobenzene, 2-NT, 4-NT, and DNT. This excellent sensing performance was credited to the profuse active sites resulting from dual doping of N and S atoms, the heightened electrical conductivity and complete exposure of the active sites of BW-NS-rGONRs after base washing action. This sensing platform was also successfully employed for TNT determination in tap water and lake water samples with an acceptable recovery% of $\sim 96.8\%$ –103.2%. Dettlaff *et al.* (2020) developed the B-doped diamond/Gr nanowall based electrochemical sensor for the recognition of TNT and TNA where this composite was synthesized by a microwave plasma-enhanced chemical vapor deposition system. The distinctive reduction peaks of both TNT and TNA were witnessed irrespective of the pH value of the electrolytic solution. The reduction peak currents were linearly related to the concentration of TNT and TNA in the range from 0.05 to 15 ppm. However, two various linear drifts were detected, accredited respectively to the adsorption processes at low concentrations up to the diffusional character of recognition for larger contamination levels. This sensor showed a limit of detection of 73 ppb and 270 ppb towards sensing of TNT and TNA respectively with good reproducibility, stability of 7 days and selectivity over inorganic ions. Furthermore, this sensor was validated through sensing of TNT and TNA in landfill leachates. Its good sensing performance was due to the high electro-active surface area of the composite. Rohaizad *et al.* (2020) demonstrated the effects of B and N doping with Gr on TNT sensing. N-doped Gr boosted the value of current in presence of TNT, while B-doped Gr exhibited the worst response as compared to the un-doped Gr. These results signify that all doping is not beneficial. But its reproducibility, stability, selectivity and applicability were not evaluated towards TNT sensing. Wang *et al.* (2020) fabricated an electrochemical TNT sensor using a hierarchical architecture composed of N-rich carbon@graphitic carbon-coated ZnO nanowire arrays on a Gr fiber (ZnO@C/GF). This composite was prepared via direct growth of a ZnO@zeolitic imidazolate framework-8 core – shell nanowire array on a GF followed by annealing. This sensor revealed a wide linear dynamic region of 0.1–32.2 μM and a low detection limit of 3.3 nM with good reproducibility, stability of 1 month and selectivity over 4-NT, DNT. Further it was employed to sense TNT in tap and lake water samples. This good sensing capability was due to the exclusive composition, enhanced conductivity, strong nitroxide – Zn interaction, and seamless interconnectivity between the components of the hybrid fiber for TNT accumulation with fast electron transference. Zhang *et al.* (2015) presented the Gr nanoribbon-supported PtPd concave nanocubes for electrochemical sensing of TNT where this composite was synthesized by the hydrothermal route. The PtPd concave cubes with an average size of ~ 11 nm were homogeneously distributed on the surface of rGO nanoribbons. Fig. 6. (a)

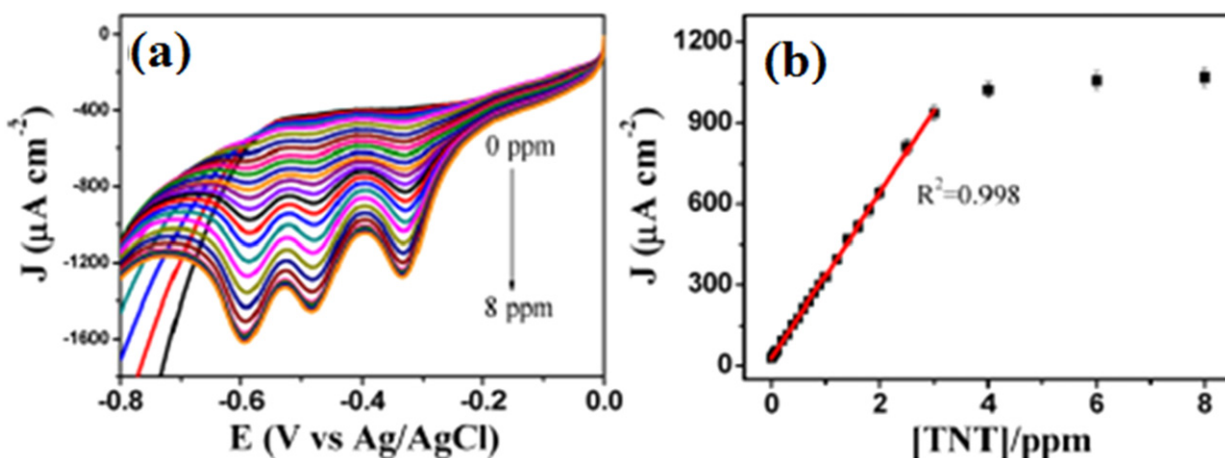


Fig. 6 (a) SVs at the Gr nanoribbon-supported PtPd concave nanocubes based sensor with various concentrations of TNT; (b) Corresponding calibration plot. Reprinted with permission from Zhang, R., Sun, C.L., Lu, Y.J., Chen, W., 2015. Graphene nanoribbon-supported PtPd concave nanocubes for electrochemical detection of TNT with high sensitivity and selectivity. *Analytical chemistry* 87 (24), 12262–12269.

Table1 List of Gr-based electrochemical sensors for environmental monitoring applications

Nanomaterial	Analytes	Sensitivity	Linear region	Detection limit	References
1. rGO-ZnO	Phenol	1.79 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ 0.389 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	2–15 μM 15–40 μM	1.94 μM	(Sha <i>et al.</i> , 2017c)
2. GO-ZnO	Phenol	-	5–155 μM	2.2 nM	(Arfin and Rangari, 2018)
3. E-rGO	Phenol	-7.6 $\Omega \text{ cm}^{-2} \mu\text{M}^{-1}$	1–40 μM	0.2 μM	(Singh <i>et al.</i> , 2016)
4. Gr-TiO ₂ -carbon paste	Phenol	-	1 μM - 0.1 M	3.66 $\times 10^{-5}$ μM	(Nurdin <i>et al.</i> , 2019)
5. Lac/AP-rGO/Chit	Hydroquin-one	14.16 $\mu\text{A mM}^{-1}$	3–2000 μM	2 μM	(Zhou <i>et al.</i> , 2013)
	Catechol	15.79 $\mu\text{A mM}^{-1}$	15–700 μM	7 μM	
6. MIP/NGNRs-IL	4-nonyl-phenol	3.4 $\mu\text{A } \mu\text{M}^{-1}$	0.04–6 μM	8 nM	(Pan <i>et al.</i> , 2015)
7. GO- CS - Ag spheres	2-CP	-	0.05–25 μM	13.9 nM	(Gan <i>et al.</i> , 2016)
	4-CP	-	0.1–35 μM	3.51 nM	
	2,4-DCP	-	0.05–35 μM	7.52 nM	
	2,4,6-TCP	-	0.03–35 μM	9.71 nM	
8. Gr-CeO ₂	TBBPA	0.021 $\mu\text{A nM}^{-1}$	0.005–1 μM	1.8 nM	(Li <i>et al.</i> , 2019)
	Catechol	0.145 $\mu\text{A } \mu\text{M}^{-1}$	0.2–10 μM	42 nM	
	DES	4.374 $\mu\text{A } \mu\text{M}^{-1}$	0.005–3 μM	1.5 nM	
	NP	7.56 $\mu\text{A } \mu\text{M}^{-1}$	0.01–2 μM	2.7 nM	
9. Polyaniline-porous polyacrylonitrile-Gr composite	p-cresol	6.46 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	2–11.6 μM	0.26 μM	(Zheng <i>et al.</i> , 2019)
10. GO - SnO ₂	4-AP	0.282 $\mu\text{A } \mu\text{M}^{-1}$	0.01–25 μM	2.2 nM	(Gan <i>et al.</i> , 2017)
	4-CP	0.107 $\mu\text{A } \mu\text{M}^{-1}$	0.02–20 μM	3.1 nM	
11. Polyaniline-Gr-carbon nanotubes composite	4-AP	2.1873 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	0.1nM - 0.01 M	63.4 pM	(Rahman <i>et al.</i> , 2018)
12. NiFe ₂ O ₄ -rGO	BPA	0.6132 $\mu\text{A } \mu\text{M}^{-1}$	0.05–25 μM	10 nM	(Bas <i>et al.</i> , 2021)
13. Au nanoparticles- MoS ₂ -IL Gr composite	BPA	4.576 $\mu\text{A } \mu\text{M}^{-1}$ 1.314 $\mu\text{A } \mu\text{M}^{-1}$	0.05–0.8 μM 0.8–4.0 μM	0.028 μM	(Wang <i>et al.</i> , 2021)
14. Laser scribed Gr	BPA	26.8 $\mu\text{A } \mu\text{M}^{-1}$	0.05–5 μM	8 nM	(Beduk <i>et al.</i> , 2020)
15. NiS ₂ -MoS ₂ -rGO composite	BPA	0.265 $\mu\text{A } \mu\text{M}^{-1}$	0.02–200 μM	0.0021 μM	(Yuan <i>et al.</i> , 2021)
16. GO- β -cyclodextrin-functionalized multi-walled carbon nanotubes composite	BPA	10.3 $\mu\text{A } \mu\text{M}^{-1}$ 0.85 $\mu\text{A } \mu\text{M}^{-1}$	0.05 – 5 μM 5 – 30 μM	6 nM	(Alam and Deen, 2020)
17. Bismuth/rGO-6	Cd ²⁺	0.2 $\mu\text{A}/(\mu\text{g L}^{-1})$	10–50 $\mu\text{g L}^{-1}$	1.2 $\mu\text{g L}^{-1}$	(Theeazen <i>et al.</i> , 2021)
	Pb ²⁺	0.4 $\mu\text{A}/(\mu\text{g L}^{-1})$		0.2 $\mu\text{g L}^{-1}$	
18. Polyaniline-alanine-rGO composite	Cd ²⁺	0.43 $\mu\text{A nM}^{-1} \text{ cm}^{-2}$	0.08–100 nM	0.03 nM	(Akhtar <i>et al.</i> , 2020)
	Pb ²⁺	0.71 $\mu\text{A nM}^{-1} \text{ cm}^{-2}$		0.045 nM	
	Cu ²⁺	0.61 $\mu\text{A nM}^{-1} \text{ cm}^{-2}$		0.063 nM	
19. rGO - silver nanoparticles	Cu ²⁺	-	10 ⁻⁹ –10 ⁻⁵ M	10 ⁻¹⁵ M	(Cheng <i>et al.</i> , 2019)
	Cd ²⁺	-		10 ⁻²¹ M	
	Hg ²⁺	-		10 ⁻²⁹ M	
20. Gr nanodots-encaged porous gold electrode	Cu ²⁺	-	0.009–4 μM	-	(Zhu <i>et al.</i> , 2015)
	Pb ²⁺	-	0.006–2.5 μM	-	
21. F-SnO ₂ /T/rGO composite	Only Cu ²⁺	0.014 $\mu\text{A nM}^{-1}$	2–1000 nM	0.3 nM	(Cui <i>et al.</i> , 2018)
	Cd ²⁺	0.009 $\mu\text{A nM}^{-1}$	20–2000 nM	5 nM	
	Cu ²⁺	0.034 $\mu\text{A nM}^{-1}$		3 nM	
	Hg ²⁺	0.014 $\mu\text{A nM}^{-1}$		5 nM	

(Continued)

Table1 Continued

Nanomaterial	Analytes	Sensitivity	Linear region	Detection limit	References
22. N@LEG	Cd ²⁺	37.47 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	5–380 g L^{-1}	1.08 g L^{-1}	(Lin <i>et al.</i> , 2018)
	Pb ²⁺	224.47 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	0.5–380 $\mu\text{g L}^{-1}$	0.16 g L^{-1}	
23. Si-doped Gr	TNT	-	-	1.2 ppb	(Niu <i>et al.</i> , 2021)
24. BW-NS-rGONRs	TNT	-	0.0008–5.1 ppm	0.1 ppb	(Zhang <i>et al.</i> , 2018)
25. B-doped diamond/Gr nanowall	TNT	-	0.01–15 ppm	73 ppb	(Dettlaff <i>et al.</i> , 2020)
	TNA	-	0.01–15 ppm	270 ppb	
26. N-doped Gr	TNT	-0.092 $\mu\text{A } \mu\text{g}^{-1} \text{ mL}$	-	-	(Rohaizad <i>et al.</i> , 2020)
27. ZnO@C/GF	TNT	-	0.1 – 32.2 μM	3.3 nM	(Wang <i>et al.</i> , 2020)
28. Gr nanoribbon- supported PtPd concave nanocubes	TNT	451.95 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0.01–8 ppm	0.8 ppb	(Zhang <i>et al.</i> , 2015)
29. Fe-enriched clay-coated rGO- N-doped polymer composite	DNT	428 $\mu\text{A mM}^{-1} \text{ cm}^{-2}$	0.02–10 mg L^{-1}	0.0016 μM	(Bairagi <i>et al.</i> , 2019)

illustrates the stripping voltammograms (SVs) of the surface of the composite based electrode towards various TNT concentrations ranging from 0.01 to 8 ppm. It was observed that at low TNT concentrations, only the first peak appeared at -0.33 V was evident. With the increasing concentrations of TNT, the other two peaks appeared serially. Hence, the first peak located at -0.33 V was used for TNT recognition. Fig. 6. (b) shows the calibration plot. This electrochemical sensor exhibited a high sensitivity of $451.95 \mu\text{A ppm}^{-1} \text{cm}^{-2}$, good linearity and a low limit of detection of 0.8 ppb with good reproducibility, selectivity over other NACs, and stability. Its practical application was tested by sensing of TNT in tap and lake water with a recovery% of $\sim 96.2\%$ – 108.5% . This excellent sensing performance of the Gr nanoribbon-supported PtPd concave nanocubes based electrochemical sensor was credited to (a) the strong charge-transfer interaction originating from efficient coordination between the unpaired electrons in d orbital of highly dispersed PtPd nanocrystals and electron-deficient TNT, (b) great capacity for the accumulation of TNT by the 1D planar structure of Gr nanoribbons, and (c) good electronic conductivity of the composite.

Bairagi *et al.* (2019) reported the Fe-enriched clay-coated rGO- N-doped polymer composite based electrochemical DNT sensor. The rGO was in situ distributed in the electro-conductive N-doped phenol/formaldehyde polymer followed by a coating of the clay 'montmorillonite' on the composite. This sensor revealed a low detection limit of $0.0016 \mu\text{M}$, good linearity over 0.02 – 10 mg L^{-1} with a high sensitivity of $428 \mu\text{A mM}^{-1} \text{cm}^{-2}$ towards DNT sensing with good repeatability, selectivity over various salts and NACs. Validation was performed through detection of DNT in seawater samples with the acceptable recovery% of 99.81% – 101.92% . This brilliant sensing performance of this sensor was accredited to (a) higher electro-active surface area of the composite (1.63 cm^2) as compared to the individual component, (b) a large number of active sites and (c) high electronic conductivity of the composite. Electrochemical sensors using Gr and its derivative have been employed widely to detect other NACs. Describing each of them is, nevertheless, beyond the scope of this article.

A summary of the reported Gr-based electrochemical sensors for environmental monitoring applications was abridged in Table 1.

Conclusion and Outlook

Gr shows exceptional electronic, physico-chemical, and optical properties, which pave an avenue for widespread applications in the field of environmental well-being. To meet the ever-expanding demands of Gr as sensing materials and its derivative GO is also becoming an advantageous and alternative sensing platform with its striking properties, including high surface area, water dispersibility, biocompatibility, easiness of chemical modification, etc. Here, we have conferred different sensing systems of Gr/GO-based electrochemical sensors for the recognition of various environmental contaminants like explosives, phenolic compounds, heavy metal ions, and so on. Even though all these electrochemical sensors display outstanding performances in terms of sensitivity, selectivity, detection limit, and repeatability, most of these developments are proof-of-concept demos only and limited within lab-based research endeavors. Numerous serious concerns and challenges still need to be taken care of. First of all, the whole performance of Gr/GO-based electrochemical sensors is influenced by the degree of oxidation, morphology, defects and number of layers of Gr-based materials. For instance, mono-layer Gr displays higher specific surface area than multilayered Gr, which provides added active sites for surface functionalization, thus confirming repeatability in the performance of electrochemical sensors. Secondly, N doping is an effective approach to increase the surface and electronic properties of pure Gr as well. N doping in mono-layer Gr makes a shift in the Fermi level, therefore dropping the density of states near the Fermi level. One of the causes, why the realization of Gr-based devices has been stimulating, is due to its absence of a bandgap. But suppression of the density of states unlocks the bandgap between conduction and valence band in N doped Gr, thus enhancing the performances of Gr-based sensors. However, the bulk fabrication of CVD grown mono-layered Gr remains the main challenge owing to its high prices. Henceforth, devoted researches need to be established for the bulk making of mono-layered Gr. Thirdly, substantial work needs to be done to the use of Gr composites in electrochemical sensors, which assists in attaining better sensing performance by combining the advantages of each constituent. To conclude, to make Gr/GO-based electrochemical sensors commercialized, the amalgamation of this sensing platform into device level is essential which is still in early stages. Constant research to tackle these challenges to allow bulk fabrication of economical Gr/GO-based electrochemical sensors for environmental applications where the sample pretreatment and incubation stages can be executed on the same platform where the recognition of analyte takes place displays huge prospective. It is only a matter of time before these concerns are fruitfully resolved, reproducible, and accessible fabrication of Gr/GO-based sensors can be effortlessly comprehended.

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Future of Energy Storage

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Environmental issues and the future decrease in the supply of fossil fuels have become the focus of serious societal debates. This has triggered great research efforts on the development of sustainable and renewable energy resources. As an essential part of the clean energy future, energy storage devices provide an efficient and versatile way to utilize clean energy in many applications. Among them, Li-ion batteries and other rechargeable batteries beyond lithium such as sodium (Na), zinc (Zn), magnesium (Mg), and aluminum batteries, so on and so forth have been considered to be the most effective and practical technologies for electrochemical energy storage. Nowadays, people's daily life has completely relied on rechargeable batteries in many crucial applications such as electric vehicles, communication equipment, multifunctional electric devices, renewable energy integration, and portable or wearable electronic devices. Therefore, developing Li-ion batteries and other rechargeable batteries with high energy density, power density, and excellent cycling performance becomes important to the future use of the technology. In terms of practical applications, power density means how fast an electrical device can be fully charged. Energy density means how long the electrical devices can be utilized after a single full charge. The batteries are typically composed of an anode, cathode, and electrolyte in order to form proper potential differences between electrodes and deliver voltage. Meanwhile, metal ions can migrate easily across the electrolyte but block electron flow internally in order to deliver output power. It means that both electrodes and electrolytes should be rationally designed in order to develop new battery systems in some specific applications, which require transient high energy output such as vehicle acceleration, blowout preventers for oil production safety, and rocket and missile launching. The development of energy storage devices depends on the different utilization purposes.

In terms of electronic devices, the future will be miniaturized, integratable, wearable, and portable devices that service multifunctional applications for either personal utilization or military purposes. Advances in portable electronic devices require the development of flexible energy devices with reliable and high-energy storage performance for long-term utilization. For personal devices such as "Google Glass", "Apple Watch" and some more emerging smart devices, powerful energy supplies that can provide enough energy for long-term utilization are required. While for military applications, an infantry platoon currently carries about 700 pounds of batteries (17 pounds per soldier) for a 72-hour mission. The situation may even become worse when new individual military equipment is equipped. Currently, most energy storage devices developed for portable devices are based on rechargeable Li-ion batteries. A critical issue facing future energy storage devices and materials is safety concerns. Safety and reliability are the dominant issues for Li-ion batteries because they cannot work properly at a temperature either above 40°C or below 0°C. At high temperatures (40–80°C), thermal runaway will take place from the carbon anode and release flammable gas through the vigorous reaction between electrode and electrolyte. At low temperature (below 0°C), lithium dendrite will be plated at the carbon electrode easily, which pierces the separator and lead to a battery internal short.

In this chapter, we will discuss the battery materials selection and design principles in order to develop new battery systems. We will introduce the basic materials science and chemistry of battery materials and how they work in the energy device. We will also introduce state-of-the-art technologies and synthesis routes to prepare battery materials for energy storage.

Solid Electrolytes for Lithium-Metal Batteries

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Abstract

The development and application of high-energy-density lithium-metal batteries to replace the traditional lithium-ion batteries are on the horizon, and solid electrolytes are the corner stones for achieving high-performance and safe lithium-metal batteries. This chapter aims to review the progress made on Li^+ -conducting solid electrolytes, including inorganic solid electrolytes, polymer solid electrolyte, and composite solid electrolytes, with an emphasis on their Li^+ conduction mechanisms, electrochemical performances, and obstacles towards practical applications in lithium-metal batteries. Besides, the current status and future directions of research and development for different types of solid electrolytes are discussed.

Introduction and Fundamental of Solid Electrolytes In Lithium-metal Batteries

Development of rechargeable batteries to replace fossil-fuel based internal combustion engines has become increasingly important. Lithium-ion battery (LIB), in particular, can offer unparalleled energy density, making it the dominant energy storage device in the market. Traditional LIBs comprise electrode materials that can host lithium ions and a liquid electrolyte (i.e., a lithium salt dissolved in organic solvents) between the two electrodes. Since the first commercialization of LIBs in the 1990s, the structure and working mechanism of LIBs have barely changed. The majority of research efforts since then have been devoted to the development of electrode materials that can stably deliver a higher voltage or host more lithium ions in order to increase the energy density of LIBs. However, the development of LIBs with higher energy densities has reached a point where even the most advanced electrode materials cannot meet the fast-growing demands for applications such as electric vehicles. A further improvement made to the LIB lies in replacing the carbon anode having a lower lithium capacity (370 mAh g^{-1}) compared to a lithium-metal anode (3860 mAh g^{-1}). A lithium-metal battery (LMB) can deliver at least 50% more energy density compared with state-of-the-art LIBs (Placke *et al.*, 2017). In fact, a lithium-metal anode has been considered as the “holy-grail” of battery research owing to its potential to offer exceptional energy density, but there is extreme difficulty to tackle a safety issue. The working principle of the LMB, despite using similar cathode materials with LIBs, relies on the reversible plating and stripping of lithium metal, which delivers higher energy density, but it also causes dendrite formation on the newly formed lithium surface during plating/stripping cycles. The lithium dendrites eventually penetrate the separator and reach the cathode, leading to an internal short circuit and consequently the ignition of a LMB. Although noticeable progress has been made to suppress dendrite formation at a lithium anode, LMBs based on a liquid electrolyte are still considered premature and unsafe for practical applications due to the flammable nature of liquid electrolytes.

Solid electrolytes (SEs) are widely recognized as the ultimate solution to the issues of lithium-metal anodes. First of all, a SE enjoys much better mechanical strength compared with the liquid electrolyte and therefore has a stronger resistance to the penetration of lithium dendrites. Second, SEs can possess a higher Li^+ transference number (LTN) than liquid electrolytes. The LTN, which is defined as the relative mobility of lithium cations to counter anions, dictates the tendency of dendrite formation; a higher LTN of solid electrolytes often results in a dendrite-free plating/stripping of lithium metal anodes – especially at high charging rates. Third, unlike liquid electrolytes that are mostly flammable, volatile, and toxic, many SEs are intrinsically safer, making them more suitable for applications in fully electric transportation. It is worth noting that LMBs based on SEs are often called all-solid-state batteries (ASSBs).

The electrochemical performances of LMBs and SEs are determined by several fundamental factors; the energy density (E) is the most critical parameter that is influenced by the voltage (V), capacity (C) and weight (m) of the battery according to Eq. 1. LMBs based on a denser and thinner SE (i.e., a SE with a lower mass) deliver higher specific energy densities, but such a SE should be sufficiently strong to separate the cathode and anode to eliminate an internal short-circuit. In practice, the energy density that a LMB can deliver is always smaller than the theoretical value due to the sluggish Li^+ transport kinetics in SEs that dictates the overall kinetics in LMBs. The Li^+ transport, quantified by the Li^+ conductivity and LTN, and the interfacial stability, identified by cyclic stability, are two factors that should be considered in designing a SE for practical applications. A widely accepted target for the Li^+ conductivity of a SE is $\sim 10^{-3} \text{ S cm}^{-1}$, which could enable operation of LMBs at room temperature (RT) without much sacrifice of their energy densities. Another critical factor is the cyclic stability of the LMB. Different from traditional LIBs, the interfacial and electrochemical instability of SEs with the anode impose a high impedance that significantly reduces the Li^+ transport at the SE/electrode interfacial contacts. Besides, the Li^+ transport in SEs is often more sensitive to temperature than in traditional LIBs, which brings about new challenges to thermal management of LMBs. Therefore, achieving a LMB with long cycle life that is comparable to the traditional LIB remains a challenging task. The electrochemical potential window, surface morphology, surface reactivity, and mechanical hardness of SEs all have profound impact on the cyclic stability of the LMB and need to be studied systemically.

$$E = \frac{C \times V}{m} \quad (1)$$

Inorganic Solid Electrolytes

The Lithium-Ion Conduction Mechanism in Inorganic Solid Electrolytes

Inorganic SEs are by far the most studied type of SE in lithium-metal batteries, and their ion-conducting mechanism in many inorganic crystals has been extensively investigated even before the invention of LIBs. For example, the beta-alumina solid electrolyte (BASE) is well-known as a ceramic fast-ion conductor for a wide variety of ions including, but not limited to, Li^+ , Na^+ , H^+ , and Pb^{2+} (Whittingham and Huggins, 1972). The energy storage devices (e.g., Na-S battery) that utilize BASE as an ion conductor work at an elevated temperature to facilitate the ionic transport through the crystal lattice. Inspired by these early discoveries, several lithium-ion conductors have been investigated. In general, the structures of ceramic fast-ion conductors are categorized as either crystalline or amorphous solids. Similar to the BASE, the Li^+ conduction mechanism in crystalline inorganic SEs relies on the hopping of lithium ions through the vacant sites in the lattice. Moreover, since most of SEs are polycrystalline, lithium ions also transport through grain boundaries, and the total Li^+ conductivity is essentially the weighted average of those two Li^+ conduction mechanisms. On the other hand, the amorphous SEs, which are also called glassy SEs, have no long-range ordering of their cations and anions. Instead, Li ions are dissociated from the anions in the amorphous solid and transport in the “ocean” of the ionic framework. The absence of grain boundaries in amorphous SEs eliminates the issue of Li^+ transport through grain boundary interfaces. However, the disordered ionic framework in amorphous SEs inhibits the full dissociation of Li ions, causing relatively a lower Li^+ conductivity compared with crystalline SEs. Nonetheless, the general thermodynamics and kinetics described in the Arrhenius equation (Eq. 2) apply for both types of electrolytes, where σ is the Li^+ conductivity, A is a predetermined constant, E_a is the activation energy for Li^+ conduction between two adjacent sites, k_B is the Boltzmann constant, and T is the temperature. Therefore, the key to the successful development of inorganic SEs with high Li^+ conductivity lies in the discovery of solids where Li^+ can diffuse through them with minimum activation energies.

$$\sigma = Ae^{\frac{-E_a}{k_B T}} \quad (2)$$

LiPON-based Thin-Film Solid Electrolytes

Lithium phosphorus oxynitride ($\text{Li}_x\text{PO}_y\text{N}_z$, LiPON) represents a category of SEs comprising Li, P, N and O with a wide range of stoichiometries. Depending on the stoichiometry and synthesis condition, the LiPON electrolyte can become either crystalline or amorphous. The first successful synthesis and application of LiPON as a SE in rechargeable batteries was realized at Oak Ridge National Laboratories in the 1990s (Bates *et al.*, 1993). To date, several approaches have been developed to synthesize LiPON, including radio frequency (RF) magnetron sputtering, (Bates *et al.*, 1993) chemical vapor deposition (CVD), (Kim *et al.*, 2013) atomic layer deposition (ALD), (Kozen *et al.*, 2015) pulsed laser deposition (PLD) (Zhao, Fu and Qin, 2002), and solid-state reactions. (Senevirathne *et al.*, 2013) The exact Li^+ conduction mechanism in LiPON still remains uncertain owing to the difficulties to characterize the amorphous structure of LiPON. Nonetheless, the structure of LiPON has been predicted by theoretical means and some advanced experimental characterizations such as neutron scattering (Lacivita *et al.*, 2018). The proposed structure (Fig. 1(a)) consists of a network of $\text{P}(\text{O},\text{N})_4$ tetrahedra with two different types of nitrogen: apical nitrogen (N_a) and bridged nitrogen (N_b). The existence of nitrogen atoms with different coordinating environments has been widely believed to be the key to the Li^+ conducting property in LiPON.

Despite different synthesis routes and stoichiometries, the LiPON electrolytes share two key properties: (i) a relatively low Li^+ conductivity typically in the range of 10^{-6} – 10^{-8} S cm^{-1} at RT and (ii) a high shear modulus that is more than ten times greater than that of lithium metal (LaCoste *et al.*, 2021). These properties endow LiPON with unique applications in thin-film LMBs. Fig. 1(b) illustrates a typical thin-film LMB made of two thin-film electrodes and a CVD-fabricated LiPON electrolyte (Dudney, 2008). The ultra-low thickness of electrodes and the LiPON electrolyte greatly reduces the Li^+ conducting resistance by shortening the diffusion path, enabling the use of LiPON as a SE despite its low Li^+ conductivity. Thanks to the high shear modulus of LiPON, lithium-metal anodes can be used in thin-film LMBs without dendrite formation and a subsequent short-circuit. The LiPON electrolyte is the only inorganic SE that realizes successful commercialization, but its application is limited to thin-film batteries due to its low Li^+ conductivity.

Oxide and Phosphate Solid Electrolytes

Garnet-type oxide electrolytes

Garnet is a family of crystals ($\text{X}_3\text{Y}_2\text{Z}_3\text{O}_{12}$) that were discovered by X-ray diffraction in the 1920s (Famprakis *et al.*, 2019), and it has been used in various applications such as laser crystals, abrasive materials, and geothermometers; however, it only recently came to light as a Li^+ conductor largely because of its strict requirement of sintering procedures and stoichiometries that had rendered it difficult to achieve a high Li^+ conductivity (Murugan *et al.*, 2007). Garnet-structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is the most well-known SE; its Li^+ conductivity can vary from 10^{-3} to 10^{-6} S cm^{-1} depending on the synthesis approach, the selection of stoichiometry, and the type and concentration of dopants. The garnet electrolyte typically has two crystal structures with a cubic or tetragonal phase, both of which are thermodynamically stable at RT. To date, two main synthesis routes have been adopted to fabricate a garnet solid electrolyte: solid-state reaction and sol-gel method; both routes lead to the garnet product with a tetragonal phase that has a lower Li^+ conductivity than the cubic phase. The introduction of dopants into the garnet structure is vital for stabilizing the cubic phase during the synthesis and thus enhancing the Li^+ conductivity. For instance, replacing 25% of zirconium (Zr^{4+}) with tantalum (Ta^{5+}) can fully stabilize the cubic phase and boost the Li^+ conductivity of the garnet electrolyte by one order of magnitude from $\sim 10^{-4}$ S cm^{-1} to $\sim 10^{-3}$ S cm^{-1} (Yutao Li *et al.*, 2012).

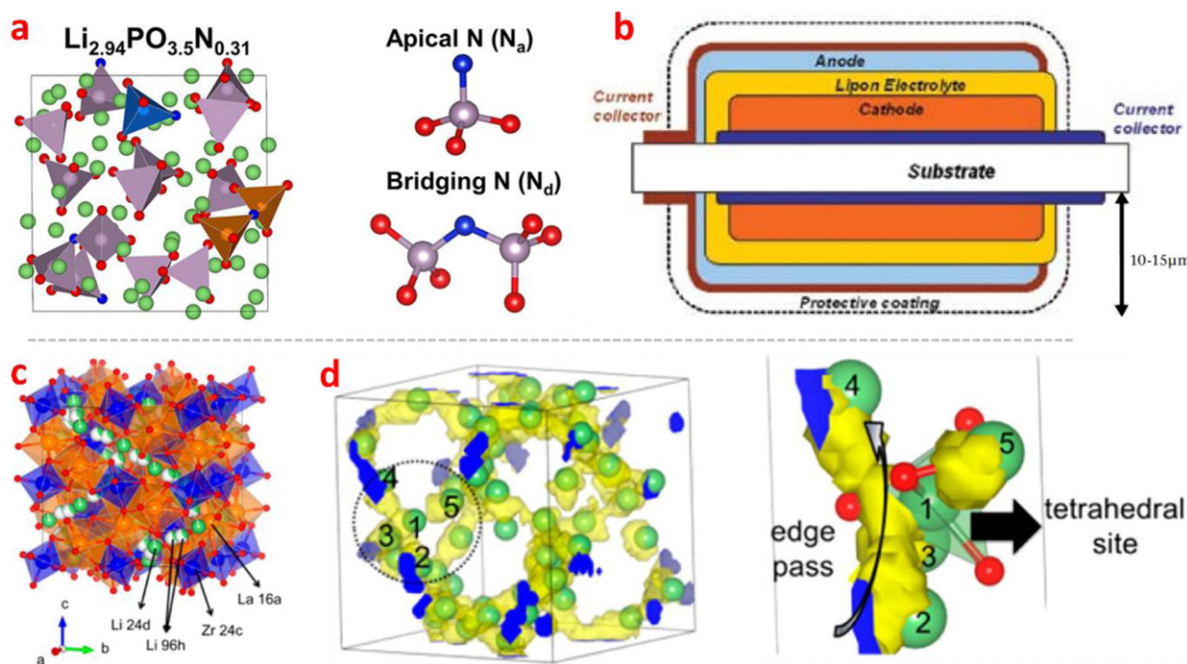


Fig. 1 (a) Schematic of AIMD-simulated $\text{Li}_{2.94}\text{PO}_{3.50}\text{N}_{0.31}$ structure. Red atoms: O, Blue atoms: N, Green atoms: Li, Light gray atoms: P; and the two different N configurations, apical and bridging. (b) Schematic cross section of a thin-film battery fabricated by vapor deposition onto both sides of a substrate support. (c) Crystal structure of cubic-type LLZO ($\text{La}\bar{3}\text{d}$); and (d) Li trajectory and enlarged view of the selected Li atoms showing the tetrahedral edge pass according to the trajectory cloud. (a) Reproduced with permission from Lacivita, V., *et al.*, 2018. Resolving the amorphous structure of lithium phosphorus oxynitride (Lipon). *Journal of the American Chemical Society* 140, (35), 11029–11038. Available at: <https://doi.org/10.1021/JACS.8B05192>. American Chemical Society. (b) Dudney, N.J., 2008. Thin film micro. *The Electrochemical Society Interface* 17 (3), (44). IOP Publishing. (c) Jalem, R., *et al.*, 2013. Concerted migration mechanism in the Li ion dynamics of garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Chemistry of Materials* 25 (3), 425–430. Available at: <https://doi.org/10.1021/CM303542X>.

Nevertheless, despite different stoichiometries in garnet electrolytes, the Li^+ conduction mechanism remains largely unchanged. Unlike most SEs, the individual Li^+ does not follow a defined path during its migration in the garnet lattice. On the contrary, the unstable residence of Li^+ at the 24d site serves as the trigger for ion mobility and the reconfiguration of surrounding Li neighbors to accommodate the initiated movement, while the Li^+ conduction is facilitated by a cooperative hopping process (Fig. 1(c-d)) (Jalem *et al.*, 2013, 2015). Such a unique Li^+ conduction mechanism provides a high room-temperature Li^+ -conducting capability to a garnet electrolyte to allow it to function as a SE in LMBs.

Apart from their high Li^+ conductivity, garnet electrolytes (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) are also electrochemically stable against reduction by lithium metal, meaning that they can be directly used in LMBs. Although garnet reacts with H_2O in a humid environment to yield an insulating LiOH or Li_2CO_3 (when CO_2 is present) layer on the SE, it can still be processed in an industrial dry room with a controlled environment. These two characteristics have made garnets one of the most promising SE candidates for commercial production of LMBs. There are, however, two major obstacles that have so far hindered the widespread application of the garnet electrolyte: (1) the lithium metal anodes have difficulty wetting the surface of the garnet electrolyte, resulting in an enormous interfacial resistance that impedes the conduction of Li^+ ; (2) similar to many oxide ceramics, garnet is prone to fracture, making it difficult to fabricate thin-film electrolytes with an appropriate processibility. Tremendous research efforts on resolving the abovementioned issues are still critical to the successful development of LMBs based on garnet electrolytes.

NASICON-type solid electrolytes

NASICON (Sodium (Na) Super (S) Ionic (I) Conductor (CONN)) is a class of structurally isomorphous 3D framework compounds that have high Li^+ and Na^+ conductivities. The NASICON compositions have the general formula $\text{AMM}'\text{P}_3\text{O}_{12}$ where the A site is occupied by alkali ions, and the M and M' sites are occupied by di, tri, tetra and penta valent transition metal ions to balance the charge condition. The phosphorous tetrahedra, which can also be partially substituted by Si, builds up the three-dimensional rigid framework of NASICON, and the interconnected channels in the framework allow the facile conduction of Li^+ or Na^+ (Fig. 2(a)) (He *et al.*, 2017). The first report of the synthesis and characterization of NASICON as a fast-ion conductor was published by Goodenough *et al.*, where the system of $\text{Na}_{1+x}\text{Zr}_2\text{P}_3-x\text{Si}_x\text{O}_{12}$ was discovered in hope to replace the BASE for energy storage and conversion applications (Goodenough *et al.*, 1976). It was later revealed that the NASICONs consisting of aluminum (e.g., $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ (LATP) and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP)) are particularly useful as SEs in LMBs because they possess high Li^+ conductivities ranging 1×10^{-4} to $3 \times 10^{-3} \text{ S cm}^{-1}$ at RT (Fig. 2(b)) (Hartmann *et al.*, 2013; Arbi *et al.*, 2015). Similar to the garnet, the synthesis of NASICON solid electrolytes typically involves a solid-state reaction or a sol-gel method where a relatively high temperature is required

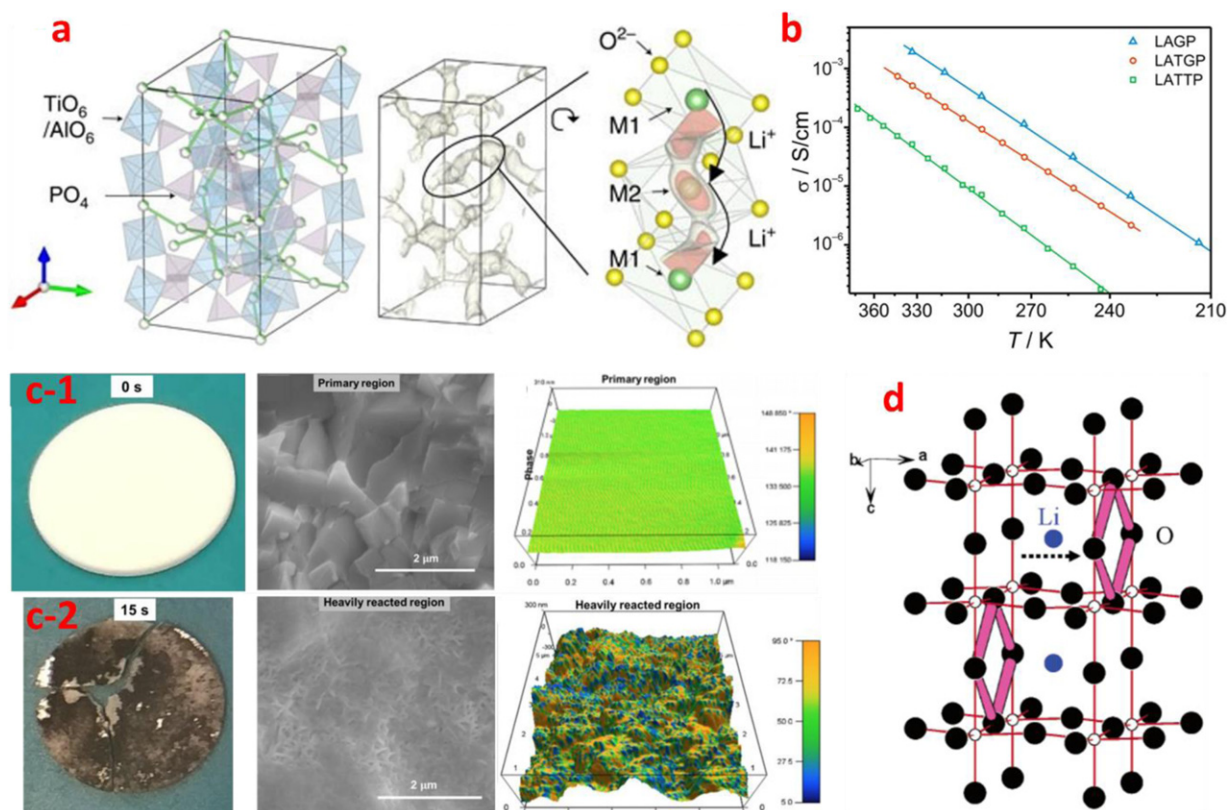


Fig. 2 (a) Crystal structures and Li^+ conducting pathways of NASICON-type LATP. (b) Li^+ conductivity of typical NASICON solid electrolytes measured by EIS. Surface images, FE-SEM cross-sectional pictures and phase separation of a LAGP pellet (c-1) before and (c-2) after 15 s contact with the molten Li metal. (d) Schematic structure of LLTO showing the pathway for the Li^+ migration. The Li, La, and vacancy are distributed at A sites. (a) Reproduced with permission from He, X., Zhu, Y., Mo, Y., 2017. Origin of fast ion diffusion in super-ionic conductors. *Nature Communications* 8 (1), 15893. Available at: <https://doi.org/10.1038/ncomms15893>. Nature Publishing Group. (b) Hartmann, P., *et al.*, 2013. Degradation of NASICON-type materials in contact with lithium metal: Formation of mixed conducting interphases (MCI) on solid electrolytes. *Journal of Physical Chemistry C* 117 (41), 21064–21074. Available at: <https://doi.org/10.1021/jp4051275>. American Chemical Society. (c) He, L., *et al.*, 2019. Failure mechanism and interface engineering for NASICON-structured all-solid-state lithium metal batteries. *ACS Applied Materials & Interfaces* 11 (23), 20895–20904. Available at: <https://doi.org/10.1021/ACSAMI.9B05516>. American Chemical Society. Stramare, S., Thangadurai, A.V., Weppner, W., 2003. Lithium lanthanum titanates: A review. *Chemistry of Materials* 15 (21), 3974–3990. Available at: <https://doi.org/10.1021/CM0300516>. American Chemical Society.

to obtain a highly crystalline and densely packed solid electrolyte with excellent Li^+ conductivity. Besides, the NASICON-type electrolytes can be made from the most earth-abundant elements, which is advantageous in terms of cost when compared with garnet electrolytes that contain rare-metal elements. Despite the excellent Li^+ conductivity, however, the application of pure NASICON electrolyte (e.g., LATP and LAGP) is very limited in LMBs mainly due to the reduction of Ti^{4+} and Ge^{4+} by lithium metal that forms a Li^+ -insulating layer that quickly results in the failure of the LMB (Fig. 2(c)) (He *et al.*, 2019). Besides, similar to garnet, NASICON-type electrolytes also suffer from a low resistance towards fracture and poor processibility. Using NASICON as an active filler material in composite-polymer electrolytes is a more common practice in LMBs and is discussed in a later section.

Perovskite solid electrolytes

The perovskite structure refers to a class of compounds that have the composition of $^{\text{XII}}\text{A}^{2+}\text{VI}^{\text{B}^{4+}}\text{X}_3^{2-}$ with the most famous example of CaTiO_3 , which was named after Lev Perovski (Katz, 2020). The perovskite has a wide range of applications with the most studied one being as the light-harvesting active layer in solar cells. The application of perovskites as a solid electrolyte is mainly based on the three-component oxide system of $\text{Li}_{3-x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) and four-component oxide system of $(\text{Li}, \text{Sr})(\text{B}, \text{Ta})\text{O}_3$. They possess Li^+ conductivities ranging from 10^{-4} to $10^{-3} \text{ S cm}^{-1}$ at RT with a LTN close to unity. The high Li^+ conductivity is due to a vacancy-induced Li^+ transport through the octahedral channels as shown in Fig. 2(d) (Stramare *et al.*, 2003). In terms of Li^+ conductivities, the perovskite electrolytes are on a par with other oxide solid electrolytes such as garnet and NASICON. The perovskite solid electrolyte suffers from chemical instability in the presence of H_2O and a narrow electrochemical stability window (due to reduction of Ti^{4+} to $\text{Ti}^{(3-x)+}$) especially at electrochemical potentials close to that of Li metal. Similar to the garnet electrolyte, the reaction between the perovskite and H_2O yields an insulating LiOH or Li_2CO_3 (when CO_2 is present) layer on the SE, which are devastating for a high Li^+ conduction. The high reactivity of perovskite SE with the Li metal has hampered its direct application in LMBs, but, similar to the NASICON electrolyte, it is often used as an active filler in composite-polymer electrolytes.

Sulfide and Halide Solid Electrolytes

Sulfide solid electrolytes

Sulfide electrolytes are generally made from Li_2S together with additives including P, Al, B, Si, Sn, Ge, Cl, and/or I with a Li to P ratio typically smaller than 0.8. Because sulfur has a much weaker interaction with Li^+ , the sulfide electrolytes show a higher Li^+ conductivity than the oxide counterparts. The structure, physicochemical property, Li^+ conductivity, and electrochemical performance of the sulfide electrolytes show a great variation depending on their stoichiometry and synthesis condition. The most widely studied sulfide electrolyte is the Li_2S - P_2S_5 glass-ceramic electrolyte prepared from Li_2S and P_2S_5 precursors that are often mechanically milled or melt-quenched into the glassy sulfide. In the glassy state, Li^+ conductivities around $10^{-4} \text{ S cm}^{-1}$ are reported. An increase in the Li^+ conductivities has been achieved by further crystallizing the glassy sulfide by an annealing process, which is ascribed to the formation of some crystalline phases (e.g., Li_7PS_6) that enhances the diffusion of Li^+ ions (Wei *et al.*, 2015). Another promising class of sulfide electrolytes that has recently attracted much attention are the so-called thio-LISICON electrolytes because their crystal structure closely resembles the γ - Li_3PO_4 LISICON. While the formula of thio-LISICON electrolyte is described as $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ ($0 < x < 1$), the crystal structures and electrochemical performances of various stoichiometries differ greatly from each other. Kanno *et al.* reported a new thio-LISICON electrolyte with the composition of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ showing a Li^+ conductivity over $10^{-2} \text{ S cm}^{-1}$ at RT, which even dwarfs that of the liquid electrolyte; (Kamaya *et al.*, 2011) such an exceptional Li^+ conductivity is a result of a crystal structure that provides one-dimensional channels with facile Li^+ transport (Fig. 3(a-b)) (Kamaya *et al.*, 2011). The high purity of precursors, the thorough mixing of precursors via high-energy mechanical milling, and air-free annealing under vacuum have been found vital for the formation of crystalline $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ with high Li^+ conductivity. The same group later reported a class of sulfide electrolyte that possess a similar crystal structure to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ by doping Si and Cl into the lattice to form a new electrolyte with a formula of $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ with an exceptional Li^+ conductivity of $2.5 \times 10^{-2} \text{ S cm}^{-1}$ (Kato *et al.*, 2016).

To date, the sulfide electrolytes show significant promise in terms of Li^+ conductivity compared with other SEs. Moreover, the sulfide electrolytes have relatively low hardness, making it easier to integrate them into LMBs without encountering interfacial contact issues. Nonetheless, there are still three critical issues facing the practical application of sulfide electrolytes in LMBs. First, the synthesis of sulfide electrolytes involves a complicated annealing process that must be carried out under a vacuum condition in a tightly sealed environment, which is challenging for scale-up production. Second, the majority of sulfide electrolytes are sensitive to moisture in the ambient due to a chemical reaction between the sulfide and water which forms a toxic H_2S product. The handling of sulfide electrolytes during the manufacturing and assembly of LMBs remains a practical challenge for their scale-up implementation. Third, although early reports suggested that sulfide electrolytes have a wide electrochemical stability window, (Kamaya *et al.*, 2011; Kato *et al.*, 2016) it later came to light that they are very reactive while in contact with most of the electrode materials including the NMC cathode and a Li-metal anode, which accounts for the low initial Coulombic efficiency and poor cyclic stability of LMBs based on sulfide electrolyte (Fig. 3(c)) (Han *et al.*, 2016).

Argyrodite-type solid electrolytes

Argyrodite is a class of crystalline compounds with the composition of $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) and cubic F43m face centered (fc) symmetry (Fig. 3(d)). (Hanghofer *et al.*, 2019) While argyrodite belongs to the sulfide family, their physicochemical property, synthesis method, and electrochemical performance differ greatly from the thio-LISICON counterparts. As depicted in Fig. 3(e), the diffusion of Li^+ in the argyrodite electrolyte follows the short-range back-and-forth transitions (48–48 h), the short-range intra-cage transitions between different 48 h pairs, and the long-range inter-cage transitions interconnecting the four cages in each $\text{Li}_6\text{PS}_5\text{X}$ unit cell. $\text{Li}_6\text{PS}_5\text{Br}$ has a slightly higher Li^+ conductivity than $\text{Li}_6\text{PS}_5\text{Cl}$, while the reported conductivities of argyrodite electrolytes are typically in the range of 1×10^{-4} to $2 \times 10^{-3} \text{ S cm}^{-1}$ (Yu *et al.*, 2021). There are two advantages of the argyrodite over the thio-LISICON electrolyte: (1) their ease of production (i.e., no need for the vacuum condition in a sealed environment) and (2) their wider electrochemical stability window. These advantages have enabled the direct application of the argyrodite electrolyte in LMBs; Lee *et al.* (2020) reported an anodeless LMB with an NMC cathode, $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte, and Ag-C composite as substrate for Li plating/stripping, which can deliver excellent cyclic stability (1000 cycles) and energy density (900 Wh l^{-1}) in a pouch cell setup (Fig. 3(f-h)).

It should be noted that the development of the argyrodite electrolyte is yet far from satisfactory. First, similar to other sulfide electrolytes, the argyrodite electrolyte is extremely sensitive to moisture, and therefore special facilities such as a dry room with dew point below -50°C is necessary for handling the argyrodite electrolyte. Second, despite some reports claiming the wide electrochemical stability window of argyrodite SEs, recent evidence has shown their instability against Li metal (Wenzel *et al.*, 2018). The in situ formed solid electrolyte interface (SEI) may be the reason for the relative stability of argyrodite electrolyte against Li metal; however, more research effort is needed to understand better the argyrodite/Li interface.

Anti-perovskite solid electrolytes

Anti-perovskite is a class of materials derived from the perovskite structure by inverting the cation and anion sublattices with a composition of ABX_3 , where A, B, and X sites are occupied by the halogen (Cl, Br, or I), oxygen, and alkali-ions (Fig. 4(a)), respectively (Dawson *et al.*, 2021). The physicochemical properties of the anti-perovskites along with their electrochemical stability window and Li^+ conductivity are very similar to those of the perovskites. The Li^+ conductivity of the anti-perovskite (e.g., typically ranges 10^{-4} to $10^{-3} \text{ S cm}^{-1}$ for Li_3OCl as the most studied anti-perovskite SE) heavily depends on the concentration of Li

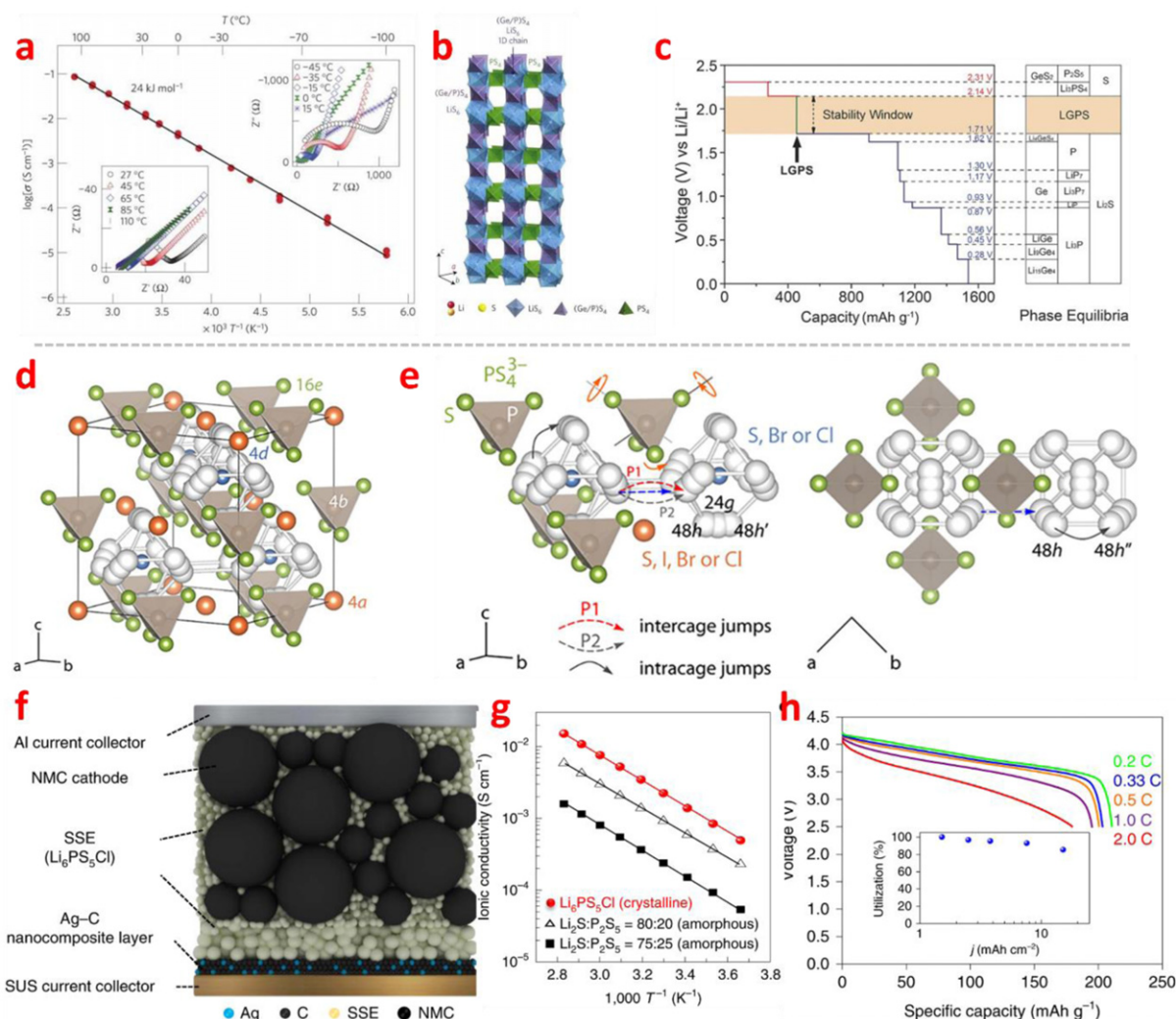


Fig. 3 (a) Impedance plots of the conductivity data (sum of the grain boundary and bulk conductivities) and Arrhenius conductivity plots of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$; and (b) framework structure of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ showing the 1D channels for facile Li^+ conduction. (c) The voltage profile and phase equilibria of LGPS solid electrolyte upon lithiation and delithiation predicted by first principles calculation. (d) Crystal structure of the argyrodite electrolyte; and (e) Li migration pathway in the argyrodite lattice. (f) Schematic of an ASSB composed of a NMC cathode, SSE ($\text{Li}_6\text{PS}_5\text{Cl}$) and a Ag-C nanocomposite anode layer; (g) Arrhenius plot of SSE ionic conductivities with temperature; and (h) rate capability of ASSBs at 60°C . (a) Reproduced with permission from Kamaya, N., *et al.*, 2011. A lithium superionic conductor. *Nature Materials* 10 (9), 682–686. Available at: <https://doi.org/10.1038/nmat3066>. Nature Publishing Group. (b) Han, F., *et al.*, 2016. Electrochemical stability of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolytes. *Advanced Energy Materials* 6 (8), 1501590. Available at: <https://doi.org/10.1002/AENM.201501590>. John Wiley & Sons. (c) Hanghofer, I., Gadermaier, B., Wilkening, H.M.R., 2019. Fast rotational dynamics in argyrodite-type $\text{Li}_6\text{PS}_5\text{X}$ (X: Cl, Br, I) as seen by ^{31}P nuclear magnetic relaxation–on cation–anion coupled transport in thiophosphates. *Chemistry of Materials* 31 (12), 4591–4597. Available at: <https://doi.org/10.1021/ACS.CHEMMATER.9B01435>. American Chemical Society. Lee, Y.-G., *et al.*, 2020. High-energy long-cycling all-solid-state lithium metal batteries enabled by silver–carbon composite anodes. *Nature Energy* 5 (4), 299–308. Available at: <https://doi.org/10.1038/s41560-020-0575-z>. Nature Publishing Group.

vacancies in the crystals due to the vacancy-induced transport mechanism of Li^+ (Fig. 4(b-c)) (Lu *et al.*, 2015; Wang *et al.*, 2020). It is reported that an appropriate degree of protonation during the synthesis of anti-perovskites is the key to achieving a high Li^+ conductivity (Fig. 4(D-e)). The presence of protons creates fast rotating hydroxy groups in the anti-perovskite lattice, providing extra space for the formation of Frenkel defects, which in turn lead to a fast and highly correlated Li^+ transport with increased Li^+ conductivity (Song *et al.*, 2018). Similar to other sulfide/halide SEs, the key to the widespread application of anti-perovskite electrolytes in LMBs depends upon the successful handling of these materials in a moisture-free environment due to their hygroscopic nature. It is worth noting that the reaction of anti-perovskite SEs with lithium metal results in a stable, Li^+ -conducting SEI, which enables the direct application of anti-perovskite SEs in LMBs (Hood *et al.*, 2016). While the interfacial stability of anti-perovskite electrolytes with cathodes in a practical LMB still requires much more study, the ability to form a stable SEI with lithium-metal anodes also renders the anti-perovskite an excellent candidate as a protective layer for other solid electrolytes that are not stable against lithium-metal anodes.

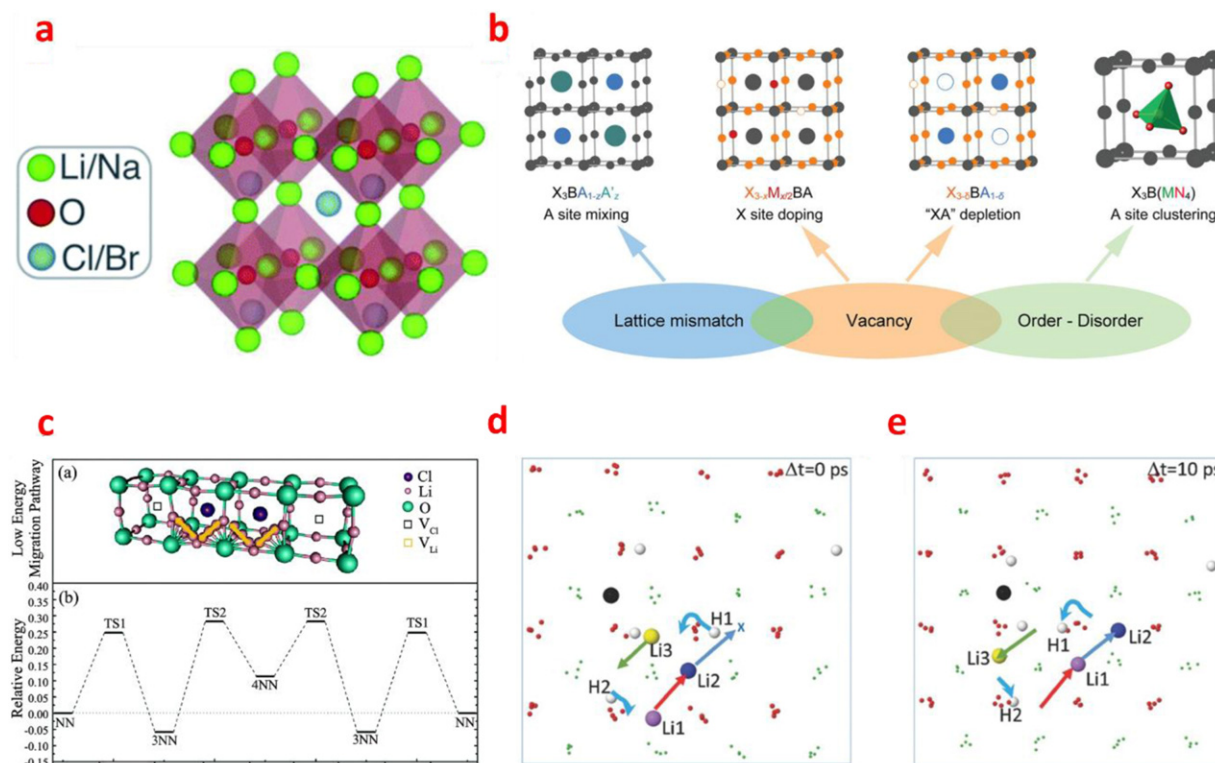


Fig. 4 (a) The crystal structure of anti-perovskite. (b) Structural design strategies for anti-perovskites toward enhanced ionic conductivity. (c) The diffusion pathway for Li vacancy and its corresponding energy profile. The snapshots of $Li_{2.92}OH_{0.08}Cl$ SE (d) before the Li^+ concerted motion and (e) after the Li^+ jumps occurred during 10 ps from BOMD simulations. (a) Reproduced with permission from Dawson, J.A., Famprikis, T., Johnston, K.E., 2021. Anti-perovskites for solid-state batteries: Recent developments, current challenges and future prospects. *Journal of Materials Chemistry A* 9. Available at: <https://doi.org/10.1039/d1ta03680g>. Royal Society of Chemistry. (b) Wang, Y., *et al.*, 2020. Antiperovskites with exceptional functionalities. *Advanced Materials* 32 (7), 1905007. Available at: <https://doi.org/10.1002/adma.201905007>. (c) Lu, Z., *et al.*, 2015. Defect chemistry and lithium transport in Li_3OCl anti-perovskite superionic conductors. *Physical Chemistry Chemical Physics* 17 (48), 32547–32555. Available at: <https://doi.org/10.1039/C5CP05722A>. Song, A.Y., *et al.*, 2018. Protons enhance conductivities in lithium halide hydroxide/lithium oxyhalide solid electrolytes by forming rotating hydroxy groups. *Advanced Energy Materials* 8 (3), 1700971. Available at: <https://doi.org/10.1002/aenm.201700971>. John Wiley & Sons.

Solid Polymer Electrolytes

The Lithium-Ion Conduction Mechanism in Solid Polymer Electrolytes

Organic electrolytes are mainly categorized into dry-polymer electrolytes (also known as solid polymer electrolytes, SPE), gel-polymer electrolytes, and liquid electrolytes, but we only include dry-polymer electrolytes in this article as they are considered as all-solid electrolytes. To date, all dry-polymer electrolytes possessing suitable Li^+ conductivity and interfacial stability for LMBs constitute oxide-based units either in their main or side chains, such as ethylene oxide in poly(ethylene oxide) (PEO), propylene oxide in polypropylene oxide (PPO), and siloxane in polysiloxane (Fig. 5(a)). Fenton *et al.* (1973) reported that ether oxygen atoms in PEO are vital for the effective dissociation of alkali salts (e.g., LiI) in PEO via the formation of alkali metal-ether complexes. The follow-up studies on PEO solid electrolytes revealed that the Li cations are complexed to the PEO chains with limited mobilities, and the conduction of Li^+ was mediated by the local motions of the complexing segments of the PEO chain (Fig. 5(b)) (Meyer, 1998). Compared to an activated ion-hopping diffusion process in inorganic ceramic electrolytes, the segmental motion in dry polymers gives a far lower Li^+ conductivity, but it can be increased considerably with increasing temperature. Since the current LMBs based on dry-polymer electrolytes require to be operated at an elevated temperature (e.g., 60°C), the development of new polymers or modifying existing polymers with higher mobility of the polymer chains (i.e., higher Li^+ conduction) at room temperature is of great interest.

Polyether Electrolytes

Polymers are well-known for their excellent processibility, which is critical for their application as SEs in LMBs because the existing facilities for the production of polymer separators (e.g., Celgard) can be utilized for the production of dry-polymer electrolytes. Furthermore, the flexibility and ease of thin-film formation of dry-polymer electrolytes enables their direct implementation in

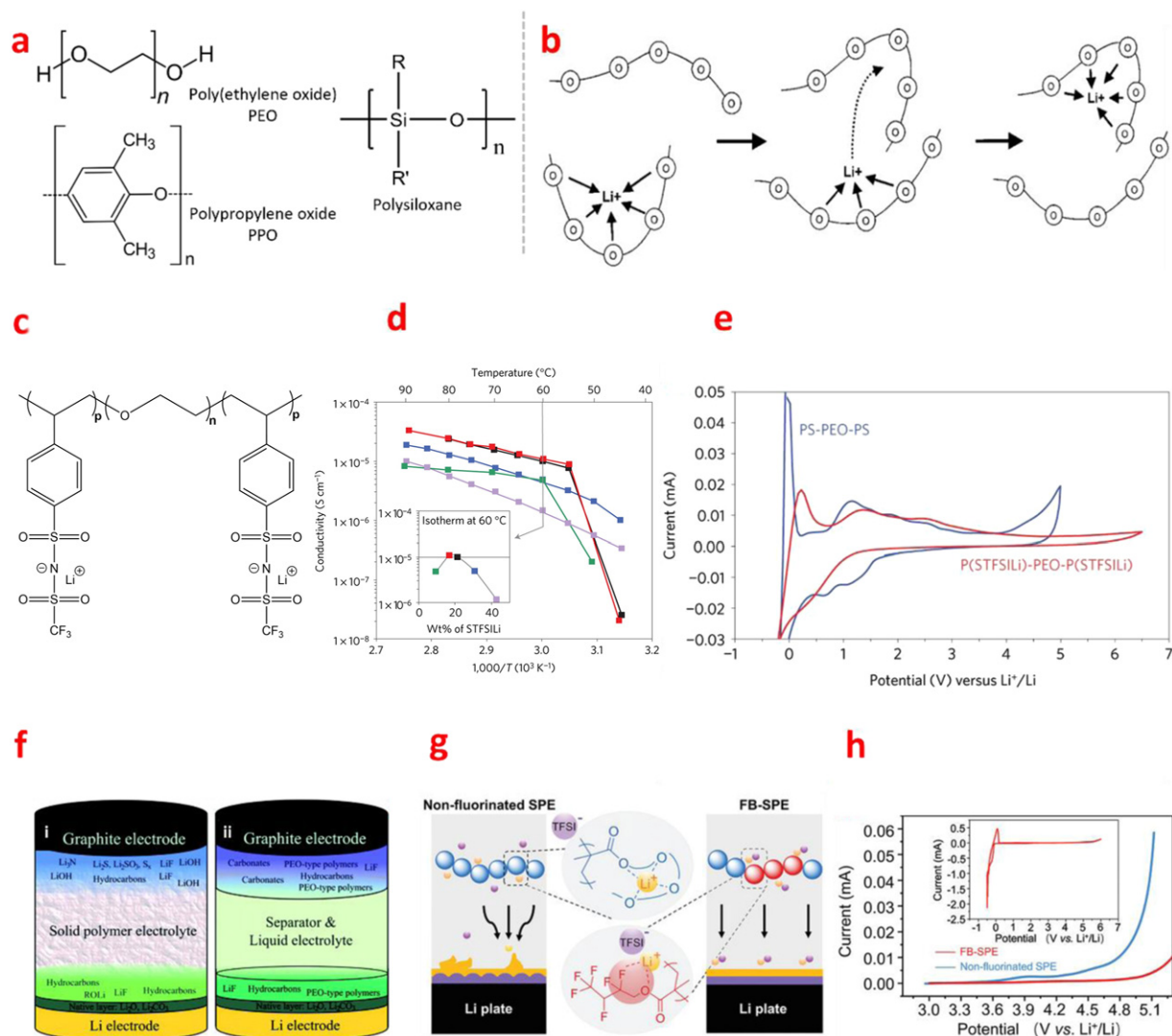


Fig. 5 (a) Chemical structure for poly(ethylene oxide) (PEO), polypropylene oxide (PPO) and polysiloxane. (b) Li⁺ conduction mechanism in PEO solid electrolyte (circles represent the ether oxygens of PEO). (c) The molecular structure, (d) plots of conductivity, and (e) linear sweep voltammetry of the single-ion conductor triblock copolymer P(STFSiLi)-b-PEO-b-P(STFSiLi). (f) Schematic representation of the compositions of the SEI layers formed in (i) SPE-based and (ii) liquid electrolyte-based half-cells. (g) Illustration of interfacial phenomena influenced by different Li⁺ coordination behavior and (h) linear sweep voltammetry of conventional SPE and fluorinated SPE, respectively. (a) Reproduced with permission from Meyer, W.H., 1998. Polymer electrolytes for lithium-ion batteries. *Advanced Materials* 10 (6), 439–448. Available at: [doi:10.1002/\(SICI\)1521-4095\(199804\)10:63.0.CO;2-I](https://doi.org/10.1002/(SICI)1521-4095(199804)10:63.0.CO;2-I). (b) Bouchet, R., *et al.*, 2013. Single-ion BAB triblock copolymers as highly efficient electrolytes for lithium-metal batteries. *Nature Materials* 12 (5), 452–457. Available at: <https://doi.org/10.1038/nmat3602>. Nature Publishing Group. (c) Xu, C., *et al.*, 2014. Interface layer formation in solid polymer electrolyte lithium batteries: An XPS study. *Journal of Materials Chemistry A* 2 (20), 7256–7264. Available at: <https://doi.org/10.1039/c4ta00214h>. Jia, M., *et al.*, 2021. Fluorinated bifunctional solid polymer electrolyte synthesized under visible light for stable lithium deposition and dendrite-free all-solid-state batteries. *Advanced Functional Materials* 31 (27), 2101736. Available at: <https://doi.org/10.1002/ADFM.202101736>. John Wiley & Sons.

LMBs similar to separators in traditional LIBs. The key to the success of dry-polymer electrolytes, however, lies upon achieving satisfactory Li⁺ conductivity and cyclic performance. The most widely studied dry-polymer electrolyte, PEO, suffers from low Li⁺ conductivity ranging from 10⁻⁸ to 10⁻⁵ S cm⁻¹ at RT, eliminating its application as a SE in LMBs. Besides, the LTN of PEO, typically ranging from 0.1 to 0.25, is even lower than the traditional liquid electrolyte, causing a high concentration polarization at high charge/discharge rates and poor battery performance. The PPO has the similar molecular structure and Li⁺ conduction mechanism as PEO, but its Li⁺ conductivity is considerably lower due to its lower dielectric constant and the existence of methyl groups hindering the complexation of Li⁺ (Meyer, 1998).

To enhance both Li⁺ conductivity and LTN, many modifications have been adapted to the PEO including tuning the molar weight and crystallinity of the PEO and a co-polymerization with other polymers to form linear, graft, or cyclic polymers (Wang *et al.*, 2021). Although significant improvements have been made using these strategies, the Li⁺ conductivity and LTN of

the PEO-based polymers are still far from satisfactory for commercial use. In a more recent strategy, single-ion conducting polymers with counter anions of lithium salt either covalently bonded to the polymer or immobilized by anion acceptors have been developed to increase the LTN; the former delivers an LTN close to unity, and the latter increases the LTN to values greater than 0.5 (Heng Zhang *et al.*, 2017). For example, Armand *et al.* developed P(STFSiLi)-b-PEO-b-P(STFSiLi) polymer electrolyte (Fig. 5(c-e)) in which anions with a highly delocalized negative charge has been covalently anchored to the backbone of a PS-PEO-PS triblock copolymer (Bouchet *et al.*, 2013). The resulting single-ion conducting polymer electrolyte has shown promising results in LMBs with a Li^+ conductivity of $1.3 \times 10^{-5} \text{ S cm}^{-1}$ at 60°C , $\text{LTN} > 0.85$, wide electrochemical stability window (up to 5 V versus Li^+/Li), and an excellent mechanical strength (10 MPa at 40°C). However, the immobilization of anions in dry-polymer electrolytes sacrifices the Li^+ conductivity dramatically, making it extremely challenging to achieve a dry-polymer electrolyte with high room-temperature Li^+ conductivity and LTN for use in practical applications.

The interfacial stability has become increasingly critical for polyether electrolytes along with their widespread application in LMBs. Most of the polyethers are neither stable against oxidation at the electrolyte/high-voltage cathode (e.g., $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$) interface nor against reduction at the electrolyte/lithium-metal anode interface, especially when lithium salts are incorporated into the polymer. Such interfacial instability issues become more evident when LMBs are operated at an elevated temperature. However, the decomposition products on the electrolyte/lithium-metal anode interface resemble the SEI layer in the traditional LIBs, acting as a protective layer to prevent further degradation of polymer electrolytes and stabilize lithium plating/stripping. In particular, the interfacial reaction between PEO electrolyte and lithium metal is found dependent on the type of lithium salt and moisture content in the electrolyte, and often yields stable compounds such as ROLi , LiF , and hydrocarbons in the PEO/Li metal interface (Fig. 5(f)) (Xu *et al.*, 2014). It is worth noting that the Li^+ conductivity at the interface is heavily influenced by the composition of the aforementioned reduction products, and more research effort should be devoted to reducing the interfacial resistance when using polyether electrolytes in LMBs. The oxidation of polyethers at the electrolyte/cathode interface, on the other hand, can be resolved by tuning the functional groups on the polymer chain to protect the ether from oxidation. For example, polyethers were fluorinated via photo-controlled radical polymerization, resulting in the anodic oxidation voltage of the resultant solid electrolyte to increase from 3.7 V to 5 V without sacrifice of Li^+ conductivity (Fig. 5(g-h)) (Jia *et al.*, 2021).

Polysiloxane Electrolytes

As mentioned in “The Lithium-ion Conduction Mechanism in Solid Polymer Electrolytes”, the Li^+ conductivity in polymer electrolytes is dictated by the mobility of the ethylene oxide polymer chain; consequently “softer” polymers (i.e., a polymer with a lower T_g) have more flexible chains and possess a higher Li^+ conductivity. Polysiloxane has a low T_g ($\sim -120^\circ\text{C}$) that is well below the operating temperature of LMBs and can deliver a much higher Li^+ conductivity compared with other polymer electrolytes such as PEO. The abovementioned theory was validated back in the 1980s right after the early report of PEO electrolyte by copolymerization of PEO with dimethyl siloxane (DMS), which resulted in a copolymer electrolyte with a Li^+ conductivity of $1.5 \times 10^{-4} \text{ S cm}^{-1}$ at DMS-EO ratio of 1:4 with LiClO_4 as the lithium salt (Nagaoka *et al.*, 1984). Another advantage of the polysiloxane electrolytes over other polymers is its exceptional thermal stability, which allows safe operation of LMBs at a temperature over 100°C ; for example, a co-polymer consisting of 3-glycidioxypropyltrimethoxysilane and PEO synthesized by hot-pressing showed a high Li^+ conductivity $1.34 \times 10^{-3} \text{ S cm}^{-1}$ at 120°C (Han *et al.*, 2015). Despite the high Li^+ conductivity, polysiloxane-based co-polymer electrolytes have not yet offered a significant improvement in their electrochemical stability at the electrolyte/cathode interface – the similar issue as with the polyether electrolyte, thus hampering the utilization of polysiloxane electrolyte in LMBs with high-voltage cathodes. The low T_g of polysiloxane electrolyte films has caused it to be easily prone to mechanical deformation, thus hindering its practical application in thin-film polymer electrolytes.

Composite Solid Electrolytes

The composite solid electrolyte (CSE) constitutes at least two different types of solids mixed with each other in a microscopic scale with well-defined interphases between adjacent phases. The dominant phase that occupies the majority of the volume is called the matrix while the secondary phase that is distributed in the matrix is called filler. Dry-polymer electrolytes and inorganic ceramics are among the most widely studied components for the CSE. On one hand, the polymer components offer the CSE its excellent processibility and interfacial contact with the electrodes. On the other hand, the ceramics remedy the poor mechanical properties (especially at elevated temperatures), low Li^+ conductivity, and LTN of dry-polymer electrolytes, giving rise to the enhanced electrochemical performances of the CSE.

The CSE fillers are categorized into inert (Li^+ insulating) and active (Li^+ conductive) fillers. The lithium conduction mechanism in CSEs depends on the type of fillers as well as the volume ratio of polymer matrix to filler. The contribution of inert fillers in CSEs to enhance Li^+ conductivity is based on two mechanisms acting cooperatively: (1) a segmental motion of the polymer chains mainly takes place in the amorphous region of the polymer matrix, while the introduction of inert fillers greatly expands the volume of amorphous region by frustrating crystalline phase formation, giving rise to increased Li^+ conductivity; (Bocharova and Sokolov, 2020) (2) the inert fillers interact with both the polymer matrix and anions through Lewis acid-base interactions; (Croce *et al.*, 1998) these interactions enhance the dissociation of lithium salts, resulting in a higher concentration of

mobile Li^+ for conduction. To expand the volume fraction of the interphase and boost the Li^+ conductivity through the abovementioned mechanisms, fillers with high surface areas are favored. Typical inert fillers include SiO_2 , ZrO_2 , TiO_2 , and Al_2O_3 nanoparticles having relative ease of synthesis and controllable sizes with high surface areas at low cost. The introduction of inert fillers with high surface area, even with a relatively small volume fraction, in turn considerably expands the highly Li^+ conducting interphases/phases and gives rise to a higher Li^+ conductivity of the CSE.

The active fillers distinguish themselves from inert fillers by their intrinsic, high Li^+ conductivity. Lithium-ion conduction mechanism in the CSEs with active fillers compared those of CSEs consisting of inert fillers have two additional mechanisms: (1) besides the Li^+ conduction through the polymer matrix, Li^+ can also diffuse through the bulk of the active filler via an activated ion-hopping process (Famprikis *et al.*, 2019) that has already been discussed in "Inorganic Solid Electrolytes"; (2) the so-called percolation theory states that the distributed ceramic fillers are interconnected with each other once the ceramic to polymer ratio reaches a certain threshold, and Li^+ can diffuse through the interconnected interphase where a space charge region forms (Fig. 6(a)) (Zou *et al.*, 2020). Due to the contribution of active fillers to the overall Li^+ conductivity of CSEs, the Li^+ conductivity of the active fillers themselves has to be considered during selection of fillers for CSEs. Typical conductive fillers include almost all the inorganic Li-ion conductors discussed in the previous sections such as garnet, NASICON, and perovskite.

Depending on the polymer to ceramic ratio, CSEs can be further categorized into either a ceramic-in-polymer CSE or a polymer-in-ceramic CSE (Fig. 6(b)) (Chen *et al.*, 2018). In the ceramic-in-polymer CSE, ceramic particles act as the filler distributed within a polymer matrix. The polymer in the CSE plays a major role in conducting the Li^+ following the same mechanisms as the dry-polymer electrolyte in CSE based on inert fillers. The polymer-in-ceramic CSEs, on the other hand, is developed aiming to fully utilize the Li^+ conduction from the Li^+ -conductive ceramic phase. The Li ions essentially transport through the ceramic frameworks as well as their interface (i.e., space charge region) with a polymer electrolyte. While the Li^+ conduction contribution of the polymer electrolyte component should not be overlooked in polymer-in-ceramic CSEs (especially at higher temperatures), the polymer mainly serves as a secondary phase to provide mechanical robustness for the CSE and facilitate better the interfacial contact between the CSE/electrodes.

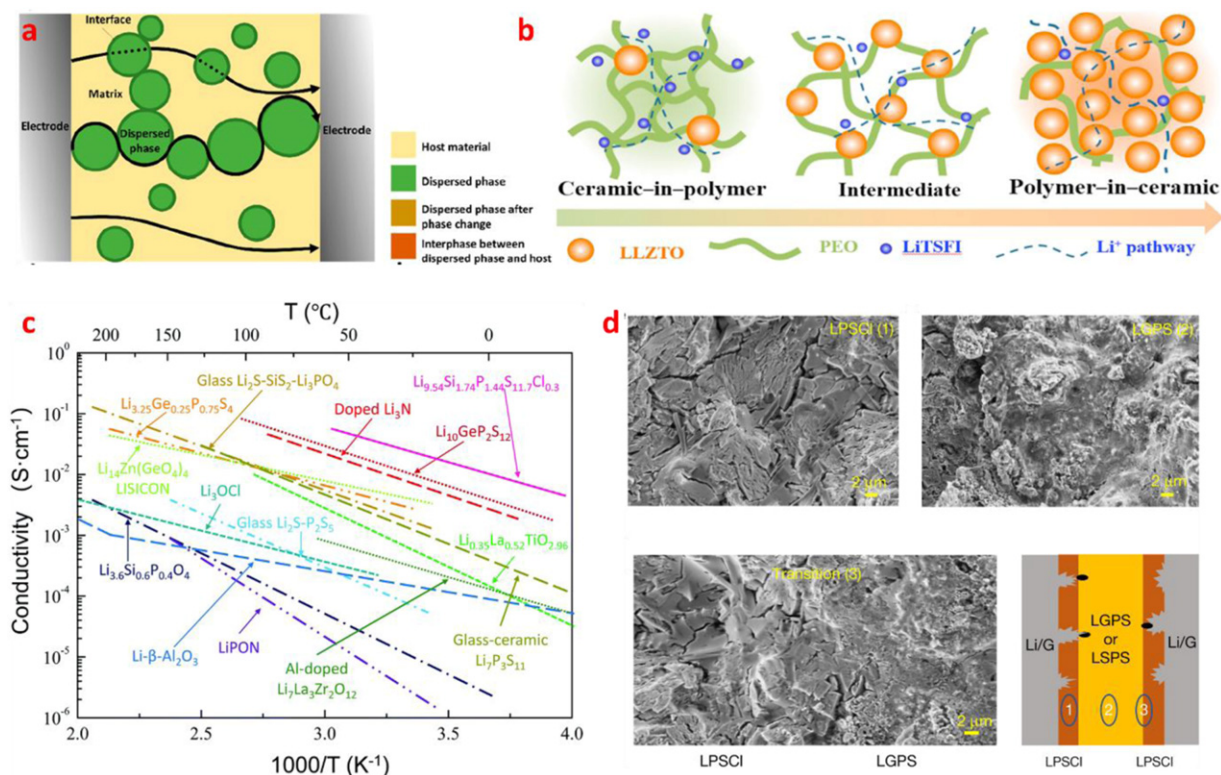


Fig. 6 (a) Illustration of ion transport in composite solid electrolytes. (b) Schematic illustration for PEO-LLZTO CSE: ceramic-in-polymer, intermediate, and polymer-in-ceramic. (c) Comparison of ion conductivity in several well-known solid lithium-ion conductors. (d) SEM images and the corresponding illustration of different cross-section regions in the multilayer design of LPSCI (1), LGPS (2) and LPSCI-LGPS (3) transition areas. (a) Reproduced with permission from Zou, Z., *et al.*, 2020. Mobile ions in composite solids. *Chemical Reviews* 120 (9), 4169–4221. Available at: <https://doi.org/10.1021/ACS.CHEMREV.9B00760>. Royal Society of Chemistry. (b) Chen, L., *et al.*, 2018. PEO/garnet composite electrolytes for solid-state lithium batteries: From “ceramic-in-polymer” to “polymer-in-ceramic”. *Nano Energy* 46, 176–184. Available at: <http://doi.org/10.1016/J.NANOEN.2017.12.037>. Elsevier. (c) Zhang, Z., Shao, Y., Lotsch, B., Hu, Y.-S., *et al.*, 2018. New horizons for inorganic solid state ion conductors. *Energy & Environmental Science* 11 (8), 1945–1976. Available at: <https://doi.org/10.1039/C8EE01053F>. Royal Society of Chemistry. Ye, L., Li, X., 2021. A dynamic stability design strategy for lithium metal solid state batteries. *Nature* 593 (7858), 218–222. Available at: <https://doi.org/10.1038/s41586-021-03486-3>. Nature Publishing Group.

Active filler-based CSEs (AF-CSEs) are by far the most studied type of CSE in LMBs due to their high Li^+ conductivity, excellent dendrite suppression capability, and exceptional processability. AF-CSEs generally enjoy 1–2 orders of magnitude increase in their Li^+ conductivity, with the highest reported value in the range of 10^{-4} to $10^{-3} \text{ S cm}^{-1}$ at RT. The key to a high Li^+ conductivity and electrode interfacial stability of AF-CSEs for their successful development relies largely on the type of active filler and polymer host, the loading and dispersion of active fillers, the surface chemistry of active fillers, and interfacial Li^+ resistance at the active filler/polymer interphase.

To date, there are several approaches to disperse fillers into the polymer matrix. The mechanical dispersion with the assistance of solvents is by far the simplest, yet most successful approach. In this technique (so called solution casting), the filler particles are dispersed into a solvent with the shear force generated either by mechanical mixing or ultrasonication; the mixture is then cast on an inert substrate to form a film after the solvent evaporates. However, agglomerations start forming inside the polymer matrix once the content of fillers increases beyond a certain threshold, that eventually impede the further enhancement of Li^+ conductivity by solely adding more fillers into the matrix. The other disadvantage of this technique is the particle aggregation – even at low loadings – due to gravity sedimentation of particles during the solvent evaporation step. Several other approaches have been developed to replace the mechanical dispersion aimed at resolving the abovementioned dispersibility issue, such as spray pyrolysis, electrospinning, and freeze-drying, but they suffer from either high cost or difficulty for scale-up production. With the Li^+ conductivity of CSEs reaching its limit by using mechanical dispersion, developing a unique yet universal approach to achieve higher filler content has become increasingly important. One way to address the dispersibility issue of a CSE is to build a Li^+ -conducting ceramic phase into a framework with an interconnected Li^+ conduction pathway, followed by filling polymers into the framework to enhance processability and mechanical stability. The Li^+ conduction in the AF-CSEs is therefore highly dependent on the connectivity of active filler particles, and a well-constructed AF-CSEs should in theory approach the Li^+ conductivity of the active filler. The majority of the AF-CSEs that possess interconnected networks of active fillers are fabricated by hot-pressing of the ceramic powders together with polymer binders, followed by adding another polymer electrolyte for better Li^+ conduction if necessary (Chen *et al.*, 2018; Jiang *et al.*, 2020). The development of the AF-CSEs with interconnected networks is still in the infant stage due to the lack of an effective method to achieve a high degree of dispersion at high filler content, and new techniques need to be developed for the fabrication of thin-film CSEs with high Li^+ conductivity and mechanical strength.

Future Directions of Solid Electrolyte Research and Development

Despite the recent research upsurge in the field of solid electrolytes, the development of LMBs is still in its early stage. A successful solid electrolyte for a LMB application must possess several key properties together, including (1) a high Li^+ conductivity comparable to that of the traditional liquid electrolyte for high-power applications such as in electric vehicles (Li^+ conductivities for typical solid electrolyte in this article are summarized in Fig. 6(c) (Zhang *et al.*, 2018)); (2) a high LTN (ideally approaching unity) to minimize the concentration polarization leading to dendrite formation at high-power rates; (3) high chemical and electrochemical stability in contact with lithium anode and cathodes; (4) high stability at the humidity levels and environmental conditions of industrial dry rooms for large-scale production; (5) the ability to form a film with thickness lower than $50 \mu\text{m}$ for maximum energy density in LMBs. After decades of research on solid electrolytes, it has been increasingly evident that none of the solid electrolytes developed so far has met all the aforementioned requirements together. For example, the garnet electrolyte has high Li^+ conductivity (e.g., $10^{-3} \text{ S cm}^{-1}$), an LTN close to unity, a wide electrochemical stability window, good inherent wettability with a lithium anode, and good stability under a low humidity environment; however, the garnet is notorious for its high hardness, making it very challenging to be incorporated into the LMBs in a practical scale.

With all the above said, the further development of solid electrolytes generally has two paths to pursue: (1) the exploration of new materials that can meet all the aforementioned requirements for them to be directly used as an electrolyte in LMBs; (2) combining different solid electrolytes on a system level to fully utilize their advantages while alleviating their weaknesses. Such combinations can be in the form of a composite electrolyte and/or a bi-layer electrolyte configuration (Huo *et al.*, 2019; Yao *et al.*, 2021). The exploration of new solid electrolytes has been a challenging task for decades and most studies are solely based on trial and error. However, the widespread application of computational design strategy has drastically changed the discovery of new solid electrolytes (Nolan *et al.*, 2018). With the maturity of first-principles calculations, the key properties of candidate materials such as electrochemical stability window, Li^+ conductivity, and mechanical properties can be readily predicted by calculations, which considerably reduces the effort needed for the experimental exploration of new solid electrolytes. Furthermore, new screening strategies such as the materials genome approach and deep learning can further accelerate the speed of computational design (Jain *et al.*, 2013; Butler *et al.*, 2018). These methods open up a new way to the rational exploration of materials for solid electrolyte applications. Even without the discovery of new solid electrolytes, the LMBs do not necessarily need to consist of only a single type of solid electrolyte, and several solid electrolytes and other additives can be integrated into a single LMB to make it function on a system level. For example, sulfide electrolytes with high Li^+ conductivity can be used as the bulk solid electrolyte while garnet or argyrodite can be coated onto the surface of a sulfide electrolyte to function as an interfacial layer for stabilizing the electrolyte/lithium-metal anode interface (Fig. 6(d)) (Ye and Li, 2021). Meanwhile, composite solid electrolytes can be mixed with cathode materials to conduct Li^+ more effectively from the bulk solid electrolyte to the cathode materials. There are several studies showing operational LMBs using the above-mentioned strategy (Lee *et al.*, 2020; Ye and Li, 2021). It should be noted that the introduction of multiple solid electrolytes will inevitably create interfaces between different solid electrolytes, and the properties of

those interfaces are still largely unknown; hence, more research effort on the system level is necessary in order to develop LMBs with multiple solid electrolytes. In coming years, it is also critical to develop new manufacturing processes, such as 3D printing techniques, for the fabrication of solid electrolytes with complex geometry and fine features for applications in nanoscaled, flexible, structural, and large-scale batteries.

Closing Remarks

LMBs have much higher energy densities compared with traditional LIBs with carbon anodes, and their successful implementation into the automotive industry would have a tremendous impact on society. To tackle the most challenging issue of using lithium metal in the LMB, switching from the traditional liquid electrolyte to a more promising solid electrolyte is almost inevitable. In this chapter, the history and recent advances of Li^+ -conducting solid electrolytes were reviewed, and our view on the future directions of solid electrolyte research and development was presented. We envisage resolving the issues facing the solid electrolyte is in sight and the successful development of LMBs based on solid electrolytes is on the horizon.

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Metal-Organic Frameworks for Advanced Battery Chemistries

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Abstract

Metal-organic frameworks (MOFs) have shown great promise for use in high-performance, next-generation batteries. MOFs benefit from several unique features, including multivariate structural components, high porosity, adjustable pore functionality, and highly periodic, crystalline structures. MOFs have been suggested as excellent platforms for the design of novel electrodes, functional separators, and solid-state electrolytes, as well as attractive materials for the regulation and improvement of physicochemical and electrochemical properties of conventional components for current batteries. In this article, the recent progress of MOFs as a fundamental materials platform for advanced battery materials are described with respect to their use as electrodes, separators, and electrolytes. Both the current challenges and future opportunities for MOFs used in the batteries are also discussed.

Key Points

- This article summarizes the recent progress of metal-organic frameworks (MOFs) as electrode, separator, and solid-state electrolyte materials for current batteries.
- The regulation and improvement of physicochemical and electrochemical properties of conventional components in batteries based on the nanoconfinement of MOFs are highlighted.
- Current challenges and future opportunities for MOFs used in the batteries are also discussed.

Introduction

The development of sustainable technology for green energy storage and conversion systems is moving forward due to the increased demand for energy resources. In this regard, the rechargeable battery technology is one of the most promising strategies for electrical energy storage. However, state-of-the-art Li-ion batteries (LIBs), based on the lithium transition metal oxide cathodes and graphite anodes (theoretical capacity: 372 mA h g^{-1}), deliver mediocre energy density ($< 300 \text{ W h kg}^{-1}$ at the cell level) (Etacheri *et al.*, 2011; Liu *et al.*, 2017b). In order to increase the energy density of conventional LIBs, various electrode materials and technologies have been developed. Especially, Li-S batteries composed of Li metal anode (theoretical capacity: 3860 mA h g^{-1}) and sulfur cathode, have drawn wide research attention, due to their very high theoretical energy density (2600 W h kg^{-1}) (Cai *et al.*, 2020a; Manthiram *et al.*, 2014). However, the electronically insulating nature of sulfur cathodes, the instability of the Li metal anodes, and the shuttling of polysulfide intermediates during charge – discharge processes present great challenges for their practical application. Therefore, the development of advanced materials is still highly desirable to improve the performance of LIBs.

Metal-organic frameworks (MOFs) are self-assembled materials through the coordination of metal ions/clusters with organic molecule ligands as linkers that have presented great promise for next-generation energy storage technologies, because of their design flexibility, framework tunability, and regular crystalline porous structures (Furukawa *et al.*, 2013; Cai *et al.*, 2020b; Zhou and Kitagawa, 2014; Cai *et al.*, 2021b). The organic – inorganic hybrid porous structures of MOFs combine both structural merits of organic and inorganic materials. For example, the intrinsically high porosities of MOFs are favorable for the electrolyte penetration, ion transportation, and storage. Moreover, the homogeneous and adjustable pore structures create the possibility of size-selective permeability. In addition, the crystalline nature of MOFs ensures well-defined structures, which paves the path to reveal the underlying structure-performance interaction in battery chemistry, and thus providing theoretical guidance for the design of advanced energy storage technologies. In summary, the versatile structural characteristics of MOFs have made these materials potential candidates for variety of essential battery components (Fig. 1) (D'Alessandro, 2016; Zhang *et al.*, 2017; Zhao *et al.*, 2018; Baumann *et al.*, 2019; He *et al.*, 2019; Li *et al.*, 2020).

MOFs with redox-active linkers or metal nodes have been recognized as promising platforms for the design of active electrode materials, while redox-inactive MOFs may prove useful as porous host materials to confine and avoid the loss of active components (D'Alessandro, 2016; Zhang *et al.*, 2017; Baumann *et al.*, 2019). In addition, MOFs have been widely used for the construction of various functional separators and solid-state electrolytes (Zhao *et al.*, 2018; He *et al.*, 2019; Li *et al.*, 2020). Recently, the confinement effect of MOFs has been extended to regulate the electrolyte behaviors of conventional liquid electrolytes, as well of the liquefied gas electrolytes (Zhao *et al.*, 2018; He *et al.*, 2019; Li *et al.*, 2020; Cai *et al.*, 2021a). Herein, we summarize recent research progress of exploring the MOFs for batteries in three categories (Fig. 1): (1) MOFs as battery electrodes; (2) MOFs as separators; (3) MOFs as electrolytes. We conclude with a discussion of current challenges and thoughts on potential research directions.

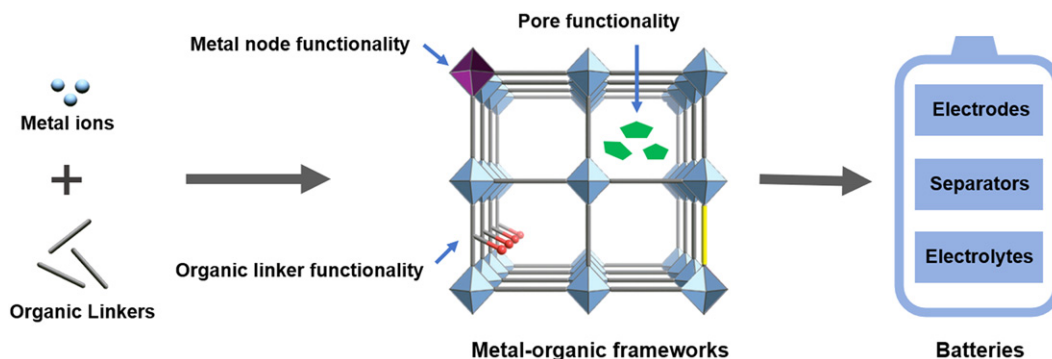


Fig. 1 Schematic showing the rational design of MOFs with desirable functions for the electrodes, functional separators, and electrolytes in batteries.

MOFs for Electrode Materials

In principle, the redox-active MOFs can be constructed through the elaborative assembly of redox-active metal ions and/or redox-active ligands. Besides, the additional redox-active species can be introduced into MOFs by impregnating as guests or post-synthetically covalent bonding. These structural and chemical diversity of MOFs may serve to enrich the domain of possible electrode materials (**Fig. 2**) (D'Alessandro, 2016; Zhang *et al.*, 2017; Baumann *et al.*, 2019).

MOFs for Cathodes

Based on the redox-active metal nodes, various Fe-based MOFs (e.g., Fe-MIL-53 (Fe(OH)BDC, BDC = 1,4-benzene-dicarboxylate), Fe-MIL-68 (Fe(OH)(BDC)(dmf)_{1,1}, dmf = *N,N*-dimethylformamide), and Fe-MIL-101 (Fe₃F(H₂O)₃O(BDC)₃) have been utilized as cathode materials (Shin *et al.*, 2015; Férey *et al.*, 2007; Fateeva *et al.*, 2010; Yamada *et al.*, 2017). During charge/discharge processes, the reversible redox cycling of Fe(III) and Fe(II) ions enable the insertion and extraction of Li⁺ ions (**Fig. 2(a)**). However, the redox reaction of metal nodes can cause changes in the metal ion coordination preferences, which results in irreversible structural rearrangement and collapse of the MOF. To balance the capacity and stability, a limited number of Li⁺ ions per Fe(III) (Li/Fe) is stored despite of high theoretical capacities. For example, when cycling between 1.5 and 3.5 V (vs Li⁺/Li), Fe-MIL-68 displays a reversible capacity of 30 mAh g⁻¹ after the insertion/extraction of around 0.35 Li/Fe, while Fe-MIL-53 with the ability of reversible storage integrating around 0.62 Li/Fe delivers higher capacity of 70 mAh g⁻¹ (Férey *et al.*, 2007; Fateeva *et al.*, 2010). Furthermore, the mesoporous Fe-MIL-101 integrating 0.62 Li/Fe reaches the capacity to 110 mAh g⁻¹ at higher cutoff voltage of 2 V, which is close to the commercial electrodes of LiCoO₂ (Shin *et al.*, 2015; Yamada *et al.*, 2017). Similarly, MOFs with diverse redox-active metal nodes (e.g., V(IV), Cu(II), Mn(II), *etc.*) have also been employed as cathode materials (Zhang *et al.*, 2014; Kaveevivitchai and Jacobson, 2015; Nagarathinam *et al.*, 2012; Zhang *et al.*, 2016). However, the low conductivity and possible structural destruction upon the change of metal valence of MOFs result in low capacities and poor cycling performances, especially at high C rates.

In order to increase the charge/discharge reversibility of MOFs, additional redox-active species have been integrated as guest molecules within the pores of MOFs. For instance, Fe-MIL-53 delivers a higher initial capacity upon encapsulation of 1,4-benzoquinone in MOF micropores (93 vs 75 mAh g⁻¹) (De Combarieu *et al.*, 2009). However, the weak interaction between the redox-active molecular guests and MOF host results in poor cycling performance due to the high solubility of quinone molecules in organic electrolytes (**Fig. 2(b)**). To address this issue, the redox-active species can be coordinately bonded to the metal nodes of MOFs. In one example, anthraquinones are bound to Zr-MOF-808 (Zr₆O₄(OH)₄(X)₆(BTC)₂, X = modulator, BTC = 1,3,5 benzene tricarboxylate) and Zr-NU-1000 (Zr₆(μ₃-OH)₈(OH)₈-TBAPy)₂, H₄TBAPy = 1,3,6,8-tetrakis(p-benzoic acid)pyrene), by taking advantage of open coordination sites on the metal nodes of these MOFs (**Fig. 2(c)**) (Liu and Thoi, 2020). However, some complex prerequisites for this strategy, including the presence of special functional groups of MOFs to bond the redox-active guests and large MOF pores to encapsulate the guest molecules, will limit the selection of MOFs and redox-active species.

As an alternative solution, redox-active organic molecules can be employed as the bridging linkers of MOFs without noticeable reducing porosity or structural integrity. It can be expected that such MOFs with both redox-active metal nodes and organic linkers can deliver higher specific capacities than those with inactive linkers. Inspired by this, Cu(2,7-AQDC) based on Cu(II) paddlewheel cluster nodes and quinone-type linkers were fabricated by the solvothermal reaction of Cu(ClO₄)₂·6 H₂O and 2,7-anthraquinonedicarboxylic acid (2,7-AQDC) (**Fig. 2(d)**) (Zhang *et al.*, 2014). Despite having a high theoretical capacity of 162 mAh g⁻¹, capacity fade from 147 mAh g⁻¹ to 105 mAh g⁻¹ was observed after 50 cycles, which was ascribed to poor conductivity and limited accessible active sites due to an inhomogeneous dispersion of MOFs in the cathodes. Later, a Mn-MOF, Mn(2,7-AQDC), was reported from the assembly of Mn(II) and 2,7-AQDC (Zhang *et al.*, 2016). In comparison with Cu(II) in Cu(2,7-AQDC), Mn(II) do not reduce to Mn(I) and thus minimizing changes at the structural metal centers during redox reactions, while it is oxidized to Mn(III) and the charges are balanced by the intercalation of anions during the charging. On the other side, during the discharge steps, the adsorbed anions are released which is accompanied by the insertion of Li⁺ ions. At the same time, the quinone-type linkers are reduced. Based on this unique “bipolar charging”

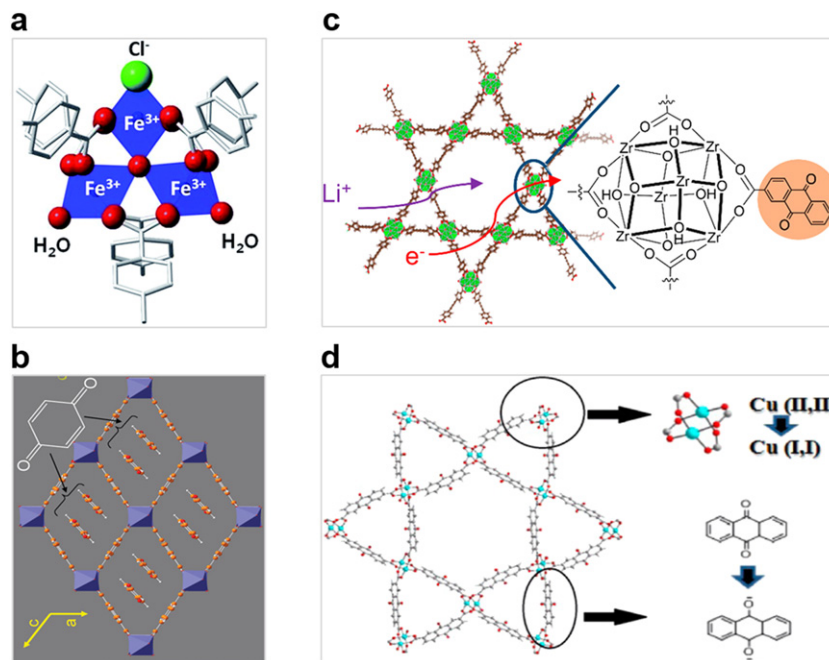


Fig. 2 Schematic illustration of MOFs as electrode materials based on (a) redox-active metal nodes. (b) active guests confined in MOF pores. (c) active species post-synthetically anchored on MOFs and (d) a MOF with both redox-active metal nodes and organic linkers. Reproduced from (a) Shin, J., *et al.*, 2015. MIL-101 (Fe) as a lithium-ion battery electrode material: a relaxation and intercalation mechanism during lithium insertion. *J. Mater. Chem. A* 3, 4738–4744. Copyright 2015 The Royal Society of Chemistry. (b) De Combarieu, G., *et al.*, 2009. Influence of the benzoquinone sorption on the structure and electrochemical performance of the MIL-53 (Fe) hybrid porous material in a lithium-ion battery. *Chem. Mater.* 21, 1602–1611. Copyright 2009 American Chemical Society. (c) Liu, B., Thoi, V.S., 2020. Improving charge transfer in metal–organic frameworks through open site functionalization and porosity selection for Li–S batteries. *Chem. Mater.* 32, 8450–8459. Copyright 2020 American Chemical Society. (d) Zhang, Z., Yoshikawa, H., Awaga, K., 2014. Monitoring the solid-state electrochemistry of Cu(2, 7-AQDC)(AQDC = anthraquinone dicarboxylate) in a lithium battery: Coexistence of metal and ligand redox activities in a metal–organic framework *J. Am. Chem. Soc.* 136, 16112–16115. Copyright 2014 American Chemical Society.

mechanism, both Li^+ ions and anions can be separately stored in the MOF pores and contribute to the overall capacity. As a result, the Mn (2,7-AQDC) cathodes exhibit a high initial capacity of 205 mAh g^{-1} and high-capacity retention at around 93% over 50 cycles.

In addition to quinone-type linkers, other organic molecules (e.g., tricarboxytriphenyl amine and tetrathiafulvalene tetracarboxylic acid) have also been utilized as the bridging linkers for the construction of redox-active MOFs (Peng *et al.*, 2016; Jiang *et al.*, 2020). Although the integration of redox-active organic materials into MOFs blocks/prevents the leaching of the active organic species and also extend the theoretical capacity of MOFs beyond single metal nodes, the practical use of these MOFs are undermined by high impedance due to the poor conductivity of the MOFs. In order to resolve this issue, a two-dimensional (2D) conductive MOF (Cu-THQ) has been constructed based on the assembly of redox-active Cu (II) and tetrahydroxy-1,4-quinone (THQ) ligands (Jiang *et al.*, 2020). The conjugated skeletons endow reasonable conductivities of $2.15 \times 10^{-3} \mu\text{S cm}^{-1}$ at 30°C . During the charge/discharge process, the Cu-THQ undergoes a four-electron transfer reaction, including a three-electron redox reaction per THQ unit and a one-electron redox reaction per copper. As a result, these MOFs exhibit a high reversible capacity and long-term cycling stability (430 mAh g^{-1} after 100 cycles).

MOFs for Anodes

MOFs serving as anodes in LIBs can be divided into two subgroups depending on the mechanisms of storing lithium ions: the conversion and intercalation mechanisms. For the conversion-type MOF anodes (Li *et al.*, 2006; Saravanan *et al.*, 2010; Han *et al.*, 2012; Liu *et al.*, 2013; Gong *et al.*, 2016; Wang *et al.*, 2017; Zhang *et al.*, 2018), using Zn-MOF-177 as an example, this MOF suffers from an irreversible conversion of Zn(II) to Zn(0), resulting in low cycling capacity and the collapse of MOF structure during lithiation steps (Li *et al.*, 2006). It is worth noting that formate-based MOFs, $\text{M}_3(\text{COO})_6$ ($\text{M} = \text{Zn(II)}, \text{Co(II)}$), enable the reversible transformation between MOFs and the corresponding metal or lithium-metal alloys, because it is more favorable for the transformation of $\text{Li}(\text{HCOO})$ to $\text{M}(\text{HCOO})_2$ rather than Li_2O (Saravanan *et al.*, 2010). Similarly, $[\text{M}(\text{croconate})(\text{H}_2\text{O})_3]_n$ ($\text{M} = \text{Mn(II)}, \text{Co(II)}$) and aluminum fumarate MOFs (Al-FumA MOFs) exhibit stable cycling behaviors (Wang *et al.*, 2017; Zhang *et al.*, 2018). However, the amorphous structures caused by the conversion of metal ions to corresponding metals creates tremendous barriers to understand the lithium storage mechanisms.

Recently, it has been found that the MOFs with benzene carboxylate-based ligands, such as HKUST-1 ($\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$), MIL-88B ($\text{Fe}_3\text{O}(\text{CH}_3\text{OH})_3\text{ClBDC}_3$), UiO-66 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6$), CuBDC, CoBDC, etc., do not follow the above conversion

mechanisms (Gou *et al.*, 2014; Maiti *et al.*, 2015; Tang *et al.*, 2016; Li *et al.*, 2016; Maiti *et al.*, 2016; Hu *et al.*, 2016; Lou *et al.*, 2017). Typically, Li^+ ions are reversibly intercalated on the organic ligands (carboxylate groups and conjugated benzene rings) while metal ions are not directly involved in the redox processes. Attributed to the integrity of metal nodes and flexible redox-active linkers during cycling, these MOFs maintain structural integrity and provide high capacity based on an organic intercalation mechanism. On the other hand, the lithium intercalation can be expected to occur on the redox-active metal nodes by the valence change rather than the conversion of metal ions. For instance, both dual redox-active Fe (III) centers and H_2BDC linkers in Fe-MIL-88B can reversibly intercalate lithium and contribute to the electrochemical capacity (Shen *et al.*, 2017).

MOFs for Functional Separators

Although MOFs have been employed as electrode materials, the poor electronic conductivity of most of the MOFs renders low energy density due to the addition of a large amount of conductive additives. By contrast, the insulating nature of MOFs is suitable for separator materials, used for preventing the short circuiting of anodes and cathodes while ensuring the diffusion of electrolytes. Based on the well-defined, porous structures of MOFs, and abundant and tailorable functional sites on the metal nodes and organic linkers (Cai and Jiang, 2017; Cai *et al.*, 2017), MOFs may serve as excellent separator materials. For example, MOFs may avoid the shuttle of active species from electrodes and adjusting the transmission of ions in the electrolyte system (Fig. 3(a) and (b)).

Avoiding the Shuttle Effect of Active Species

During the charge/discharge processes, some electrode materials or their intermediates (e.g., organic electrodes, polysulfides) are soluble in electrolytes, resulting in the leaching of active materials and undesirable side reactions. The incorporation of ionic sieves derived from crystalline porous materials as separators has been recognized as a solution to prevent the leaching of active species while allowing the diffusion of Li^+ ions (Fig. 3(a)). For this purpose, various membrane materials based on MOFs have been developed to take advantage of their size-selective permeability (Cai *et al.*, 2020b).

Microporous HKUST-1 with a pore size of 0.9 nm was the first MOF-based separator to block the leaching of polysulfides (Li_2S_n , $4 < n \leq 8$) (Bai *et al.*, 2016). To assemble MOF powders into membrane materials, flexible graphene oxide (GO) nanosheets were

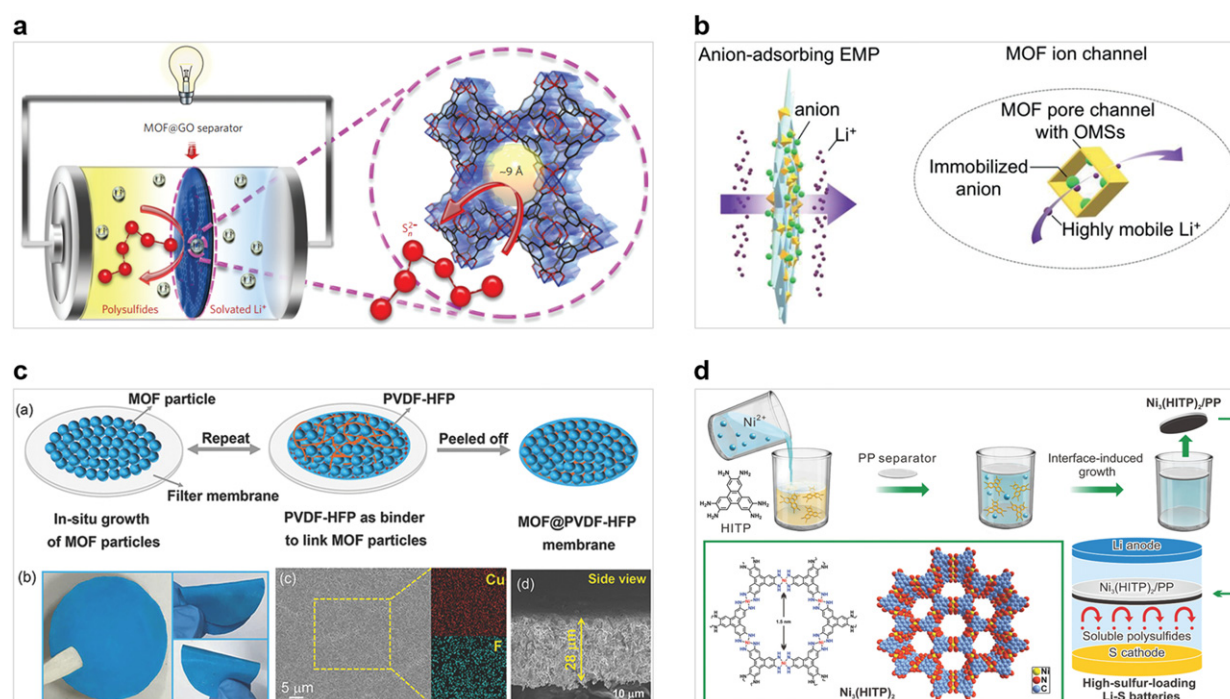


Fig. 3 Schematic showing the mechanisms of MOFs to (a) avoid the shuttle effect of active species in batteries and (b) modulate the transportation of Li-ions. (c) Self-supporting mixed matrix membranes (MMMs) based on the mixing of polymer binders and MOF NPs. (d) The crack-free MOF membranes through interface-induced in-situ growth method. Reproduced from (a) Bai, S., Liu, X., Zhu, K., Wu, S., Zhou, H., 2016. Metal-organic framework-based separator for lithium-sulfur batteries. *Nat. Energy* 1, 16094. Copyright 2016 Nature Publishing Group and 2019 John Wiley & Sons, Inc. (b) Zhang, C. *et al.* 2019. Anion-sorbent composite separators for high-rate lithium-ion batteries. *Adv. Mater.* 31, 1808338. (c) He, Y., *et al.*, 2018. Simultaneously inhibiting lithium dendrites growth and polysulfides shuttle by a flexible MOF-based membrane in Li-S batteries. *Adv. Energy Mater.* 8, 1802130. Copyright 2019 John Wiley & Sons, Inc. (d) Zang, Y., *et al.*, 2018. Large-area preparation of crack-free crystalline microporous conductive membrane to upgrade high energy lithium-sulfur batteries. *Adv. Energy Mater.* 8, 1802052. Copyright 2018 John Wiley & Sons, Inc.

parallelly filtered with HKUST-1 nanoparticles (NPs) to form robust MOF@GO membranes. Using the resultant microporous membranes as the separators, Li-S batteries showed enhanced long-term cycling stability. However, the compromise between the fast kinetic of redox reactions and the suppression of the shuttle effect is hard to avoid based on the physical sieves. Later, polystyrene sulfonate (PSS) threaded HKUST-1 membranes were grown in situ on Celgard membranes to ensure the fast Li^+ ion transport (Guo *et al.*, 2018). Owing to the high Li^+ ionic conductivity of PSS, the PSS@HKUST-1/Celgard membranes effectively block polysulfides without the trade-off of redox kinetics. Inspired by the above strengths of $-\text{SO}_3^-$ groups in Li-S batteries, $-\text{SO}_3\text{H}$ or $-\text{SO}_3\text{Li}$ functional MOFs (UiO-66- SO_3H or UiO-66- SO_3Li) were subsequently utilized for the construction of functional separators. The introduction of negative sulfate groups not only promotes the diffusion of Li^+ ions, but also contributes to blocking the polysulfides by the electrostatic repulsion. Similarly, several membranes based on MOFs with negative or polar groups have been developed for Li-S batteries, such as Mn-BTC with free COO^- groups and UiO-66- NH_2 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC}-\text{NH}_2)_6$) with polar $-\text{NH}_2$ groups (Suriyakumar *et al.*, 2018a,b; Kim *et al.*, 2018; Wang *et al.*, 2020).

Unfortunately, due to the intrinsic poor processability of MOF NPs, the MOF-based membranes can become mechanically brittle. To address this issue, self-supporting mixed matrix membranes (MMMs) were fabricated by mixing MOFs with robust polymer binders (Fig. 3(c)). Owing to combining the good processability of polymers and selective permeability of MOFs in MMMs, the resultant HKUST-1/PVDF-HFP membranes are flexible enough to satisfy the high requirements of durability and stability in Li-S pouch cells (He *et al.*, 2018). Recently, a versatile strategy has been developed for the large-scale preparation of MOF-based porous MMMs (Gao *et al.*, 2020). By the in situ heat-assisted solvent-evaporation process, porous MMMs with various MOFs and polymers can be rapidly produced.

Despite of excellent molecular sieving ability and flexible membrane structures, the membranes formed by the assembly of MOF NPs generally accompany with undesired cracks or voids, caused by the agglomeration of MOF NPs or poor compatibility between MOFs and polymers/substrates. Therefore, the direct fabrication of continuous and phase pure MOF membranes is highly desirable for crack-free MOF membranes. Motivated by this, an interface-induced growth method has been developed for the in situ growth of a conductive $\text{Ni}_3(\text{HITP})_2$ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene) layer on commercial Celgard separator (Fig. 3(d)) (Zang *et al.*, 2018). With a low/thin coating layer (0.066 mg cm^{-2}), such MOF membrane significantly improves the rate and cycling performance of Li-S batteries. Later, a flexible and ultrathin MOF membrane has also been reported by the vacuum filtration-assisted assembly of MOF nanosheets (Tian *et al.*, 2019). Although MOF crystals are generally fragile, the van der Waals interactions between ultrathin nanosheets enable excellent mechanical flexibility of the self-supporting MOF nanosheets-assembled membranes. Recently, a sol-gel strategy has been developed to achieve a self-standing ZIF-8 ($\text{Zn}(\text{mim})_2$, Hmin = 2-methylimidazole)-gel membrane without using any binders or substrates (Bai *et al.*, 2020). Serving as separators for rechargeable organic batteries, the crack-free MOF-gel separators exhibit excellent permselective capability in blocking the leaching of specific organic intermediates.

Controlling the Transmission of Electrolyte Ions

In addition to blocking the leaching of active species, the size-selective permeability of MOFs has been used to regulate the transportation of electrolyte ions (Fig. 3(b)) (Zhang *et al.*, 2019; Li *et al.*, 2021; Valverde *et al.*, 2020; Shen *et al.*, 2019; Han *et al.*, 2019; Liu *et al.*, 2017a). Due to the bulkier solvation sheath of Li^+ , effective conduction of Li^+ only accounts for a small portion of total ionic conductivity. Considering that anions in the electrolytes of LIBs generally do not engage in the lithiation reactions, the low Li^+ ion transference number (t_{Li^+}) leads to concentration polarization and dendritic Li deposition, etc. To address this issue, MIL-125- NH_2 ($\text{Ti}_8\text{O}_8(\mu_2-\text{OH})_4(\text{BDC}-\text{NH}_2)_6$)-modified membranes were employed as the separators for Li-S batteries (Liu *et al.*, 2017a). The MOFs not only served as molecular sieves to block the permeability of polysulfides but also suppressed the growth of lithium dendrites, attributed to the increased t_{Li^+} through the interaction of polar groups (e.g., $-\text{NH}_2$) on the organic linkers and electrolyte ions. For example, an anion-sorbent composite separator was achieved based on UiO-66-based MMMs (Fig. 3(b)) (Zhang *et al.*, 2019). After activation at elevated temperature to remove terminal moieties on uncoordinated metal sites, the open metal sites in UiO-66 selectively fixed the anions, thereby improving the t_{Li^+} . To further improve the t_{Li^+} , the same group demonstrated a method for in situ growth of UiO-66- NH_2 on glass fiber separators (Shen *et al.*, 2019). As a result, the MOF-modified separators showed a 100% increased t_{Li^+} (0.67 vs 0.32), and thus improved the performance of lithium metal anodes. Recently, a quasi-solid electrolyte membrane was developed by using high loading of MOFs (80 wt%) (Li *et al.*, 2021). Due to the strong interaction of UiO-66 and polybenzimidazole (PBI) polymer binders, the formed flexible and self-supporting UiO-66/PBI membranes are capable to directly work as the battery separators, which not only ensure the excellent long-term stability of lithium metal anodes but also improve the oxidation resistance of electrolyte towards high-voltage cathodes.

Benefitting from the strong adsorption ability of MOFs, the MOF-based membranes can be promising absorbent to trap the hazardous species in electrolytes formed during the cycling processes (Chang *et al.*, 2020b). For example, the presence of water in electrolytes introduced during battery fabrication will generate hydrofluoric acid (HF) that attacks the electrodes during electrochemical cycling processes, thereby leading to the decomposition of electrolyte and severe capacity degradation. Recently, a MOF separator was reported as a in-built water scavenger. Owing to the high porosity and strong complex interaction of water and open Cu(II) sites on HKUST-1, the MOF separator can efficiently suppress the attack of HF and the dissolution of transition metals.

MOFs for Electrolytes

The possible leakage, high flammability, and low Li^+ ions transfer number of organic liquid electrolytes lead to poor battery performance and safety issues. Although solid-state electrolytes (SSEs) can avoid the above issues, the low ionic conductivity at an ambient condition and poor compatibility between SSEs and electrode limit their practical applications. Owing to their unique structural features MOFs show great promise for the design of excellent SSEs, the regulation of common liquid electrolyte behaviors, and even lower the vapor pressure for liquefied gas electrolytes (Fig. 4) (Cai *et al.*, 2021a; Zhao *et al.*, 2020; Miner and Dincă, 2019).

Ion-conductive MOFs

MOFs have been recognized as a versatile platform for the design of excellent SSEs. To achieve the desired conductivities, various strategies have been developed for the construction of highly ion-conductive MOFs (Fig. 4(a)). For instance, a solid lithium electrolyte was achieved by integrating lithium isopropoxide with $\text{Mg}_2(\text{dobdc})$ ($\text{dobdc} = 1,4\text{-dioxido-2,5-benzenedicarboxylate}$), in which coordinatively unsaturated $\text{Mg}(\text{II})$ sites promote the uptake of the lithium isopropoxide (Wiers *et al.*, 2011). Owing to the electrostatic interaction between open metal sites and alkoxide anions, they delivered a conductivity of 0.31 mS cm^{-1} and activation energy of 0.15 eV. Subsequently, the same group reported *tert*-butoxide (LiOtBu)-grafted UiO-66, where the uncoordinated $\text{Zr}(\text{IV})$ sites were utilized to bind the OtBu^- anions (Ameloot *et al.*, 2013). In addition to modifications at the metal nodes, the organic ligands of MOFs have been modified to anchor anion groups. For example, a post-synthetic modification (PSM) method was used to covalently graft the trifluoromethylsulfonyl (Tf) groups on the amino groups of UiO-66- NH_2 (Zhu *et al.*, 2019). This single ion conductor shows a high t_{Li^+} (0.84) and moderate conductivity (0.207 mS cm^{-1}) at 25°C . Similarly, a $-\text{SO}_3\text{Li}$ group containing UiO-66 was achieved by using SO_3H functional linkers (Chiochan *et al.*, 2020). After mixing with Li-based ionic liquids, the resulting MOF-based SSE exhibits a conductivity of 0.33 mS cm^{-1} at ambient condition. An ion-conductive Cu-azolate MOF was reported based on a reversible neutral-to-anionic redox transition (Park *et al.*, 2017). This stoichiometric transformation allows the loading of large amount of cations (e.g., Li^+ , Na^+ , Mg^{2+}) to balance the charge of MOFs. Later, the same group investigated the influence of softness of the halide ions and valence of metal ions toward the ion-pairing strength in various metal halide incorporated MOFs (Miner *et al.*, 2019). They demonstrated that MOF-LiCl showed a higher Li^+ transference number than MOF-LiBr (0.69 vs 0.34), and MOF-LiCl, MOF- MgCl_2 , MOF- AlCl_3 delivered gradually decreased conductivities.

MOF-Confined Ionic Liquids

To improve the conductivity of MOF-based SSEs, various ionic liquid (IL) containing lithium salts have been incorporated with MOFs, due to the negligible vapor pressure, nonflammability, wide electrochemical window, high ionic conductivity, and thermal stability of ILs (Fig. 4(b)). For instance, Fujie and Kitafawa *et al.* investigated the phase behavior and ionic conductivity of Li^+ -doped ILs loaded ZIF-8 (Fujie *et al.*, 2015). They demonstrated the diffusion of Li^+ ions in the micropores of the MOF through the exchange of the solvating anions. To address the interfacial issues of SSEs and electrodes, a Li^+ -containing, IL impregnated MOF-525 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{TCPP-H}_2)_3$, $\text{TCPP} = 4,4',4'',4'''$ -(porphyrin-5,10,15,20-tetrayl) tetrabenzoate) was reported (Fig. 4(b)) (Wang *et al.*, 2018). After integrating this solid-like electrolyte with a LiFePO_4 cathode and Li metal anode, the solid-state batteries (SSBs) showed excellent capacity retention at a wide working temperature range (-20 to 150°C). Similarly, UiO-66 and UiO-67 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BPDC})_6$, $\text{BPDC} = 4,4'$ biphenyl-dicarboxylate) were also utilized to encapsulate the ILs (Liu and Sun, 2020; Wu and Guo, 2019b).

Li-IL loaded MOFs have been recognized as promising candidates as fillers to enhance the performance of polymer-based SSEs. Nano-sized MOF-5 ($\text{Zn}_4\text{O}(\text{BDC})_3$) has been used to improve the electrochemical performance of poly(ethylene oxide) (PEO)-based SSEs (Yuan *et al.*, 2013). Owing to the rich Lewis-acidic sites on the surface of MOF-5 NPs, the strong interaction between MOFs with PEO chains and lithium salts reduce the crystallization of PEO and increase the lithium salt solubility. Similarly, Li-IL loaded UiO-66 were employed as the fillers of PEO-based SSEs (Huo *et al.*, 2019). In addition to improving the conductivity and suppressing the crystallinity of PEO, the fillers enhance their stabilities towards Li metal. To promote the adsorption of ILs and improve the Li^+ ionic conductivity, a cationic MOF by the post-synthetic modification of a mixed-linker-based MOF (Wu and Guo, 2019a). After employing it as the filler of PEO-based SSEs, the interaction of $-\text{NH}_2$ groups on the MOFs with ether oxygen atoms of the PEO polymers enable high electrochemical stability up to 4.97 V, while the cationic skeleton of the MOF immobilizes anions and guides the uniform distribution of Li^+ ions.

Lean Liquid Electrolyte Filled MOFs

Considering the opposing merits and demerits of liquid and solid electrolytes, the confinement of liquid electrolytes within MOFs represents an intriguing route to address this dilemma. Inspired by the functions of ionic channels in biological systems (Fig. 4(c)), a class of pseudo solid-state electrolytes was fabricated via complexing the anions of a liquid electrolyte (LiClO_4 in PC) on HKUST-1 (Shen *et al.*, 2018). The strong complexation of uncoordinated $\text{Cu}(\text{II})$ sites of the MOFs with ClO_4^- anions

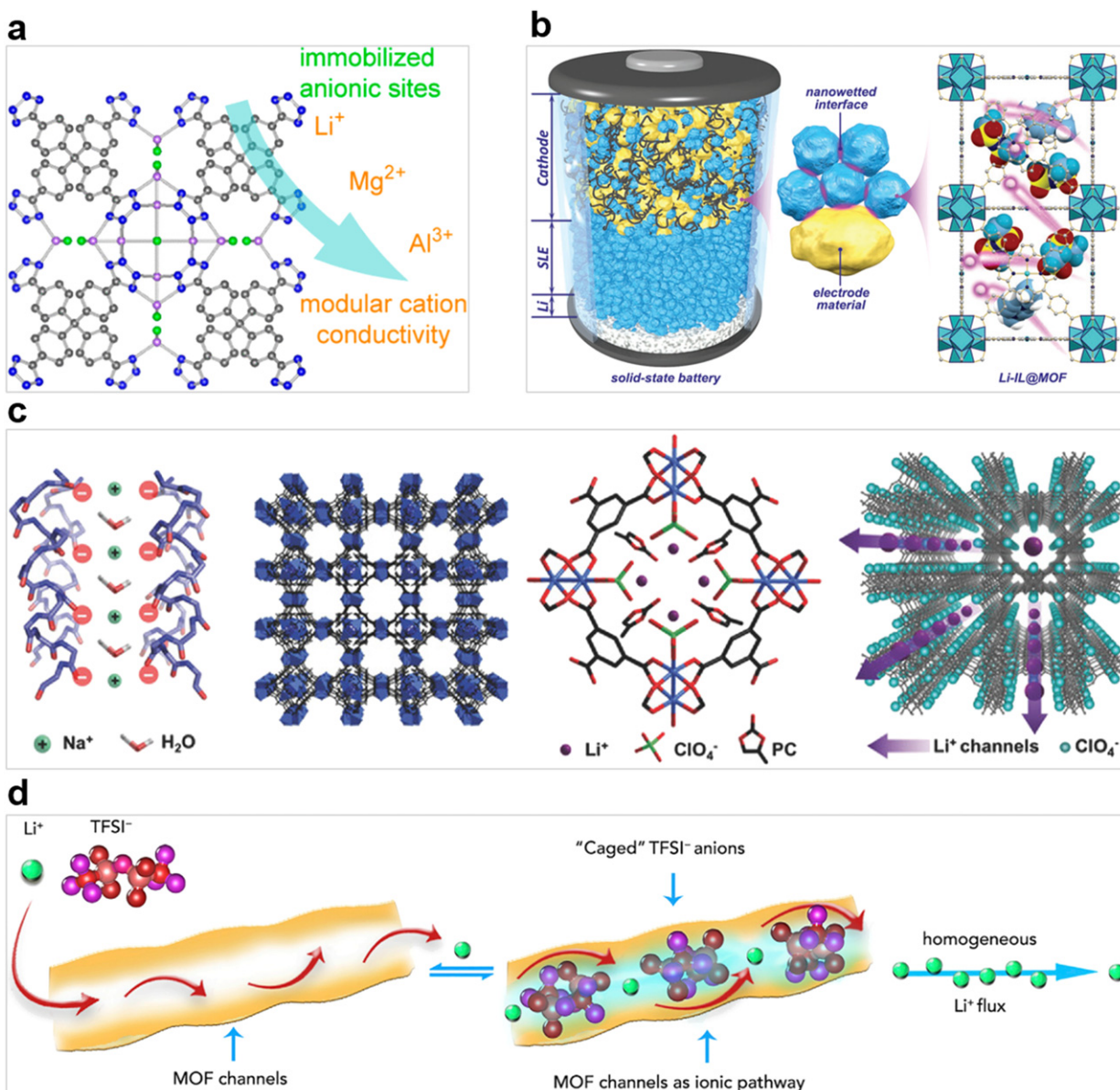


Fig. 4 Schematic illustration of MOF-based solid electrolytes based on: (a) neat MOFs. (b) MOF/ionic liquid composites and (c) MOF confined lean liquid electrolytes. (d) The proposed mechanism of MOFs to improve the Li-ions transfer behavior. Reproduced from (a) Miner, E.M., Park, S.S., Dincă, M., 2019. High Li^+ and Mg^{2+} Conductivity in a Cu-azolate metal–organic framework. *J. Am. Chem. Soc.* 141, 4422–4427. Copyright 2019 American Chemical Society. (b) Wang, Z., *et al.*, 2018. A metal–organic-framework-based electrolyte with nanowetted interfaces for high-energy-density solid-state lithium battery. *Adv. Mater.* 30, 1704436. Copyright 2017 John Wiley & Sons, Inc. (c) Shen, L., *et al.*, 2018. Creating lithium-ion electrolytes with biomimetic ionic channels in metal–organic frameworks. *Adv. Mater.* 30, 1707476. Copyright 2018 John Wiley & Sons, Inc. (d) Bai, S., *et al.*, 2018. High-power Li-metal anode enabled by metal-organic framework modified electrolyte. *Joule* 2, 2117–2132. Copyright 2018 Elsevier Inc.

from the liquid electrolyte weakens the interactions of the anions with Li^+ ions in liquid electrolyte, thereby enabling fast Li^+ ion conduction through the channels of HKUST-1. Similarly, the ionic sieving effect of HKUST-1 was extended to facilitate the homogeneous flux of Li^+ ions (Fig. 4(d)), ensuring stable plating/stripping of lithium metals even at higher current density of 10 mA cm^{-2} (Bai *et al.*, 2018). Later, another group reported used Cu-MOF-74 ($\text{Cu}_2(\text{DHBDC})(\text{H}_2\text{O})_2$, DHBDC = 2,5-dihydroxyterephthalate) for encapsulating various liquid electrolytes (Yuan *et al.*, 2019). They demonstrated that the immobilization of anions on open metal sites of MOFs change the Li^+ migration behaviors and thus enable a dendrite-free Li metal battery. In addition, they also proved that the presence of Cu-MOF-74 suppresses the dissolution of Mn(II) ions for high voltage Li// LiMn_2O_4 batteries.

Recently, the confinement of MOFs has been extended to regulate the solvation behavior of liquid electrolytes. An unique “frozen-like” solvent, de-solvated Li^+ ion, and crystal-like salt solute behavior of ether-based electrolyte was recently proven in

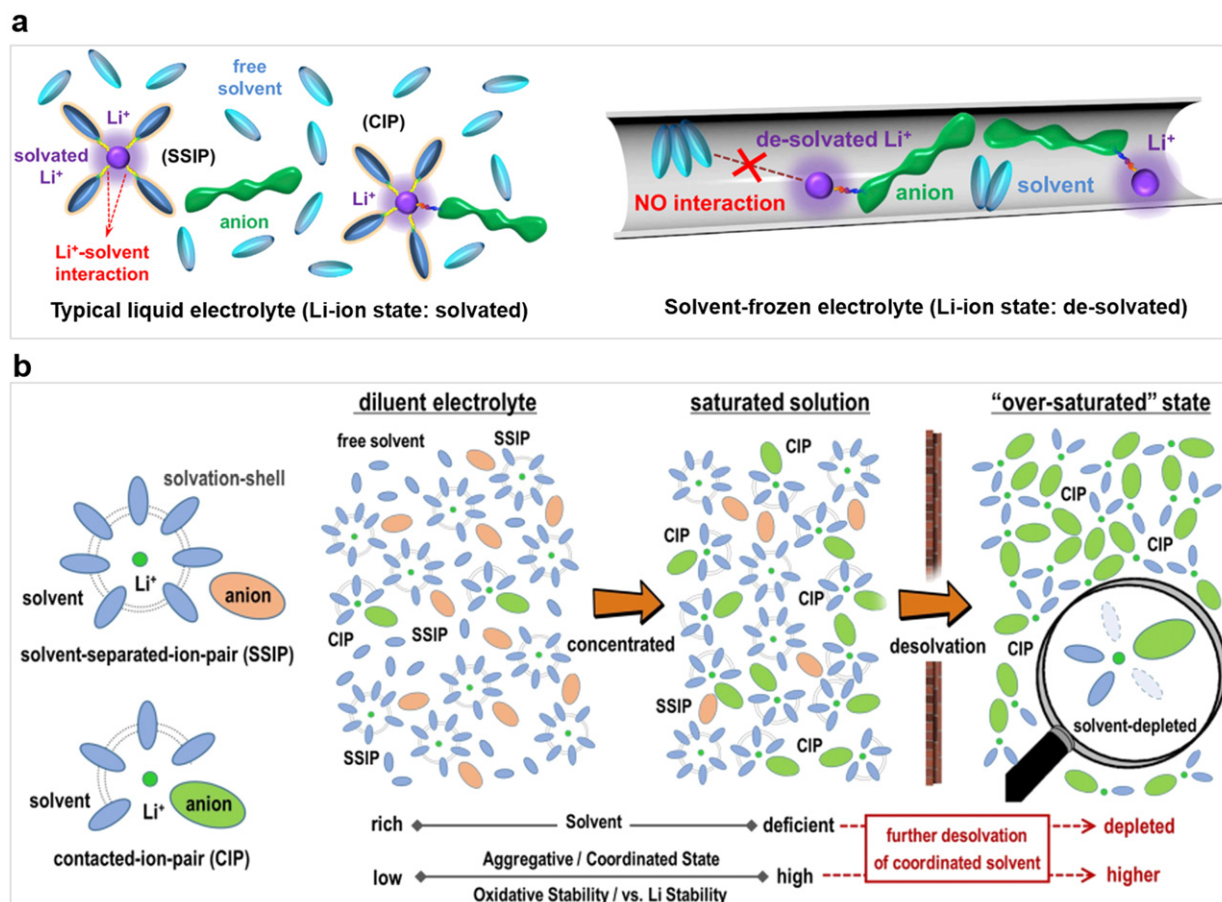


Fig. 5 Schematic illustration of (a) solvent-frozen and (b) "over-saturated" state of conventional liquid electrolytes in the nanopores of MOFs. Reproduced from (a) Chang, Z., *et al.*, 2020. A liquid electrolyte with de-solvated lithium ions for lithium-metal battery. *Joule* 4, 1776–1789. (b) Chang, Z., *et al.*, 2020. Beyond the concentrated electrolyte: Further depleting solvent molecules within a Li^+ solvation sheath to stabilize high-energy-density lithium metal batteries. *Energy Environ. Sci.* 13, 4122–4131. Copyright 2020 Elsevier Inc. and The Royal Society of Chemistry 2020.

the ZIF-7 ($\text{Zn}(\text{bim})_2$, bim = benzimidazolate) nanopores (Fig. 5(a)) (Chang *et al.*, 2020a). This electrolyte configuration enabled the conventional ether-based electrolyte stable for high-voltage (4.5 V) LIBs. In addition, the same group employed MOFs to deplete the solvent molecules within Li^+ solvation structures (Fig. 5(b)) (Chang *et al.*, 2020c). Owing to the narrow nanochannels of HKUST-1, more aggregative configuration of electrolytes were achieved compared with highly concentrated electrolyte system. This unique confined system thereby enlarged electrochemical stability windows of conventional electrolyte from 4.5 V to 5.4 V.

MOF Confined Liquefied Gas Electrolytes

Apart from the above solid and liquid electrolytes, liquefied gas electrolytes (LGEs) developed by the Meng group have been recognized as promising energy storage systems operating at ultra-low temperatures (e.g., below -30°C), because of their unique physicochemical properties including facile ion transport from ultra-low to ambient temperatures, extremely low melting points, etc., (Rustomji *et al.*, 2017). Generally, an extremely high internal pressure is adopted to condense gas molecules into a liquid state, thereby dissolving the Li salt to ensure a decent ionic conductivity. The high vapor pressure does create potential safety concerns for practical applications. To address these concerns, the sub-nanometer confinement of MOFs was able to reduce the actual pressure required to condense gas molecules for LGEs (Cai *et al.*, 2021a). To endow the capillary condensation of microporous MOFs to the battery chemistries, a novel "brick-and-mortar"-like strategy has been developed to construct a series of mechanically flexible MOF-polymer membranes (MPMs), in which microporous UiO-66 served as the porous "brick" while the polymer binders (PVDF) functioned as the mechanically flexible "mortar" (Fig. 6). When using these MPMs as the separators and LGEs as the electrolytes, the lithium/fluorinated graphite batteries produced a high capacity ($\sim 500 \text{ mAh g}^{-1}$) even at -40°C and reduced pressure (70psi). On the contrary, the cells with the conventional Celgard membranes delivered negligible capacity with a value of $\sim 0.03 \text{ mAh g}^{-1}$.

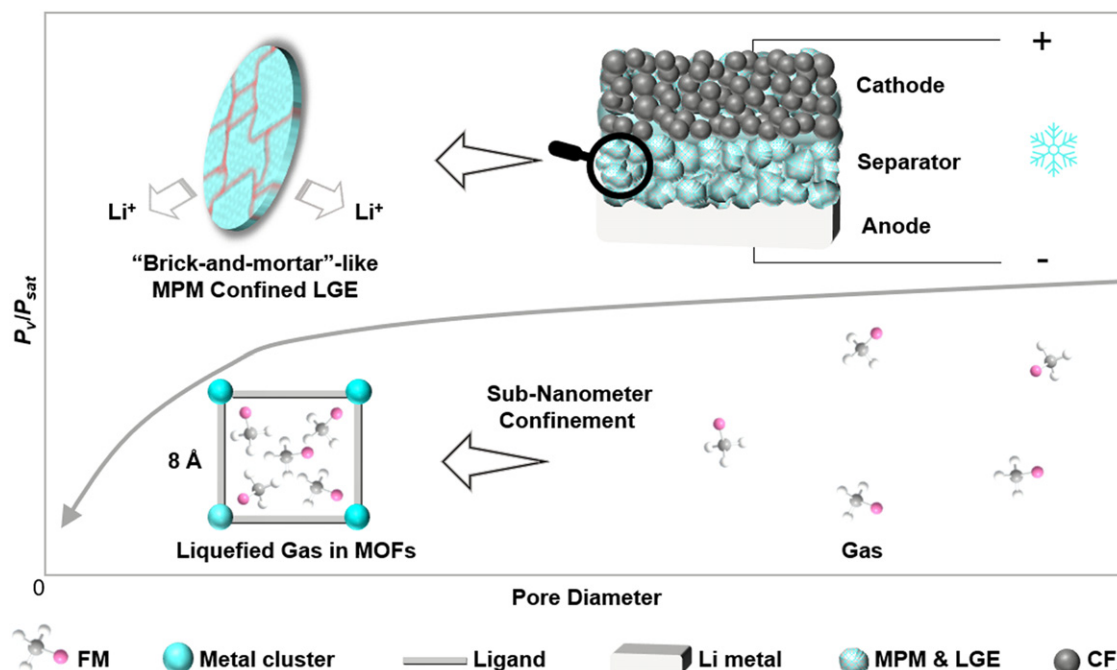


Fig. 6 Schematic illustration of MOFs to lower the equilibrium pressure of liquefied gas and the implementation of MPM-confined LGE system for Lithium batteries. Reproduced from Cai, G., *et al.*, 2021a. Sub-nanometer confinement enables facile condensation of gas electrolyte for low-temperature batteries. *Nat. Commun.* 12, 3395. Copyright 2021 Springer Nature.

Conclusions and Outlook

In conclusion, the application of MOF materials for advanced battery chemistries, covering MOF-based electrodes, separators, and electrolytes has been presented. Owing to the unique structural strengths, MOFs have been recognized as excellent candidates for the design of novel materials and improving the performance of conventional battery components. Although great progress has been achieved, the use of MOFs for advanced battery chemistries is still in its early stages. Several challenges remain to be resolved before their practical applications.

- (1) The capacities of redox-active MOFs are still not satisfied to meet the demand of high energy-density batteries. These can be attributed to three aspects: (1) narrow working voltage range and low theoretical capacities caused by low density of active sites; (2) mediocre redox stability of MOFs, which renders lower practical capacities than their theoretical values and poor long-term cycling performances; (3) poor ionic and electronic conductivities, leading to high overpotentials and high demand of conductive additive, thereby reducing the practical energy density. Therefore, the construction of conductive MOFs with abundant redox-active sites and excellent electrochemical stability is highly desirable for potential practical applications of MOF-based electrodes.
- (2) For the MOF-modified separators, a large volume of inactive MOFs is generally introduced to ensure compacted and flexible structures of MOF layers on the selected substrates. Therefore, the thickness and mass loading of MOFs need to be minimized in order to reducing the trade-off energy density of practical cells. For self-supporting MOF membranes, their mechanical properties are still highly dependent on the addition of polymer binders. Pure MOF-based membranes with crack-free, thin, and flexible features, which are superior to commercial separators, are highly desirable but challenging to achieve.
- (3) Despite that MOFs have been widely employed as host materials or functionalized fillers for the construction of various SSEs, the resulting conductivities are still not matching with the level of traditional liquid electrolytes. In addition, the interaction between host-guest and the detailed mechanism of ion transmission is still unclear. Benefitting from the crystallinity of MOFs, future work should focus on the study of underlying structure-properties relationship, thereby providing guidance for the design of excellent SSEs based on other materials.
- (4) The application of nanopore confinement in MOFs for conventional electrolytes has been an emerging research topic. Some unique electrolyte behaviors, e.g., agglomerated solvation structures, enlarged electrochemical stability windows, and increased mobility of Li^+ ions relative to anions, have been reported in the pores of MOFs. More exciting properties toward battery chemistries should be explored based on the structural features of various MOFs, such as reticular chemistry, engineering defective sites, multivariable components, and adjustable pore functionality. More insightful elucidation of structure-properties relationship can be expected by integrating the computational simulation with experimental approaches.

With continuous endeavor and extensive collaborative of different research fields (e.g., chemistry, material science, engineering, and energy) for the above challenges, we are confident that the MOFs should present a promising future for various advance batteries.

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Ion Intercalation Process in MXene Pseudocapacitors With Aqueous and Non-Aqueous Electrolytes

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Abstract

The 2D transition metal carbide and nitride MXenes, especially titanium carbide, are ideal electrode materials for pseudocapacitors due to their metallic conductivity, open interlayer space, and redox-active surface. This article summarizes the electrochemical ion intercalation processes in MXene-based pseudocapacitors with both aqueous and non-aqueous electrolytes. We discuss the impact of ion intercalation on the interfacial characteristics of MXenes, such as interlayer space, surface groups, and interfacial ion-solvent arrangement. Furthermore, we reveal the importance of ion accessibility on the overall pseudocapacitive performance of MXenes and summarize the general strategies to facilitate ion intercalation.

Key Points

- The general structure of MAX phases and MXenes.
- The MXenes synthesis is classified into Fluorine-based and non-Fluorine-based methods.
- The charge storage mechanisms and the performance of MXene-based electrodes in aqueous electrolytes.
- The charge storage mechanisms and the performance of MXene-based electrodes in non-aqueous electrolytes.
- Strategies to avoid the restacking of 2D layers and facilitate the interfacial ion transport in MXenes.

Introduction

There are ever-increasing demands for high-power electrochemical energy storage (EES) systems to balance the electricity grids with intermittent renewable energy sources. Meanwhile, EES systems with high power density shorten the recharge time, which is crucial for many applications, such as portable electronic devices and electric vehicles (Pomerantseva *et al.*, 2019; Tarascon and Armand, 2001; Yang *et al.*, 2011). Among all EES devices, batteries provide high energy density as they store energy through Faradic redox reactions with at least one electron charge transfer. However, the redox reactions are accompanied by phase transformation, limiting the power density and cycling stability of batteries (Tarascon and Armand, 2001). In comparison, electrical double-layer (EDL) capacitors exhibit high rate capability and long cycling life as they store charges electrostatically through reversible adsorption of electrolyte ions at the electrode/electrolyte interface (Simon and Gogotsi, 2020; Wang *et al.*, 2012). Due to the absence of Faradic contribution, the energy density of EDL capacitors is moderate, generally $< 10 \text{ Wh kg}^{-1}$.

Pseudocapacitors can achieve a much higher charge storage capacity than EDL capacitors as the charge transfer process occurs across the electrode/electrolyte interface (Fleischmann *et al.*, 2020). Unlike the diffusion-controlled process observed in batteries, the pseudocapacitive charge storage process is surface-controlled (Simon and Gogotsi, 2008). In general, there are two types of pseudocapacitive charge storage mechanisms: surface redox and pseudocapacitive intercalation (Choi *et al.*, 2020). The surface redox reaction is observed on the thin-Film RuO_2 , which delivers an ultrahigh volumetric capacitance with high rate capability (Augustyn *et al.*, 2014). But the cost of RuO_2 electrodes is too high for practical applications. Pseudocapacitive intercalation, which occurs in orthorhombic-phase Nb_2O_5 (Augustyn *et al.*, 2013) and TiO_2 (B) (Laskova *et al.*, 2014), involves rapid ion intercalation and extraction without phase transformation of the electrode materials. However, these pseudocapacitive electrodes are usually operated at rates lower than that of the EDL capacitors, as their low electrical conductivity increases the resistance of electrodes.

MXenes, a group of 2D early transition metal carbides/nitrides, have shown great potential as high-rate pseudocapacitive electrode materials due to their high electrical conductivity, redox-active surface, and open interlayer with good ion accessibility. The general chemical formula of MXenes is $\text{M}_{n+1}\text{X}_n\text{T}_x$, where M stands for the transition metal, X is Carbon and/or Nitrogen, and T_x represents the surface functional groups (e.g., $-\text{F}$, $-\text{Cl}$, $-\text{OH}$, and $=\text{O}$) (Naguib *et al.*, 2014). So far, more than 30 MXenes have been synthesized experimentally (Fig. 1(a)), and among which $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is the most studied one (Gogotsi and Huang, 2021). In one layer of $\text{Ti}_3\text{C}_2\text{T}_x$, the interleaved Ti and C layers form a transition metal carbide core and two metal oxides/hydroxide surfaces, offering efficient electron transport pathways and abundant redox-active sites (Lukatskaya *et al.*, 2015). Surface redox

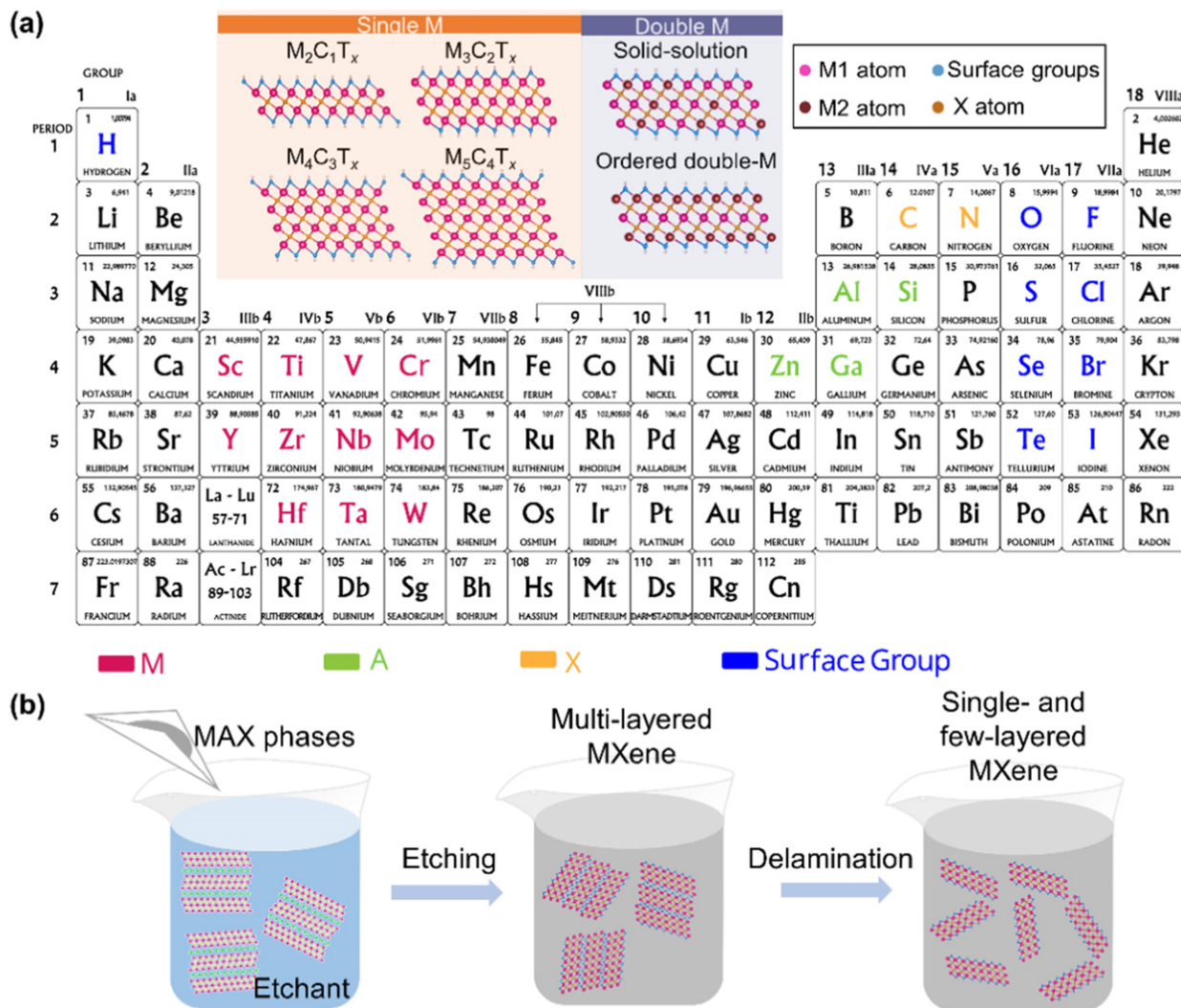


Fig. 1 (a) Periodic table showing the elements that are involved in MAX phases and MXenes. Color code in the periodic table: red (transition metal), yellow (X element), blue (surface groups), and green (A element in MAX phases). Schematics show the general structures of MXenes. (b) Schematic illustration of the typical synthesis process of MXenes from MAX phases in solution.

reactions occur during proton intercalation in $\text{Ti}_3\text{C}_2\text{T}_x$ leading to ultrahigh volumetric capacitance and excellent rate capability with H_2SO_4 electrolyte (Lukatskaya *et al.*, 2017).

It is appealing to increase the thickness of MXene electrodes and use less-corrosive non-acidic electrolytes for practical applications. However, increasing the electrode thickness leads to the restacking of 2D layers, which impairs ion accessibility and enlarges ion transport resistance (Ghidiu *et al.*, 2014). The ion transport resistance also increases as the size of the intercalated ions is larger than the proton. Additionally, using non-acidic aqueous electrolytes, especially the non-aqueous electrolytes, or replacing $\text{Ti}_3\text{C}_2\text{T}_x$ with other MXenes, generally leads to weaker surface redox and lower capacitance. (Lukatskaya *et al.*, 2013) To improve the electrochemical performance of MXenes in various electrolytes, researchers focus on investigating the charge storage mechanism in MXenes and designing MXene-based electrodes with different compositions and structures. This article discusses the ion intercalation process in MXene-based pseudocapacitors with various electrolytes and summarizes the strategies to maximize the ion accessibility with an improved electrochemical performance of MXenes.

Fundamentals: The General Structure of MAX Phases and MXenes

MAX phases, the precursors of MXenes, are a group of layered ternary compounds with a space group symmetry of $\text{P6}_3/\text{mmc}$. The general formula of MAX phase is $\text{M}_{n+1}\text{AX}_n$ ($n = 1, 2, 3, 4$), in which M stands for early transition metal (such as Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo), A represents elements from groups IIIA and IVA in the periodic table, and X is C and/or N (Barsoum and Radovic, 2011;

Eklund *et al.*, 2010; Sun, 2011). Typical MAX phases show close-packed hexagonal structure, in which X layers and M layers are alternately arranged to form a layer of $M_{n+1}X_n$, and a layer of A atoms is interleaved between two $M_{n+1}X_n$ layers (Fig. 1(b)).

Multilayer $M_{n+1}X_nT_x$ MXenes are synthesized by chemical etching the A layer from the corresponding MAX phases (Alhabeib *et al.*, 2017; Naguib *et al.*, 2011). The selective removal of A layer from MAX phases is possible since the bond between M-A is more chemically active than M-X. Notably, the MXenes etched from the MAX phases with excess aluminum show fewer defects on the MXene flakes and higher electrical conductivity (Mathis *et al.*, 2021). Based on the composition of the M-layer, MXenes can be classified into three different categories: single-M element, M-site solid solution, and ordered double-M elements (Anasori *et al.*, 2017). A second M element can replace the outer M-layer or inner M-layer of single-M element MXenes and forms ordered double-M elements MXenes. Meanwhile, M-site solid solution MXenes contain at least two M elements uniformly distributed in the M-layer. When the number of M elements is more than 4, the MXene is called the high-entropy MXenes. Compared to the normal MXenes, the high-entropy MXenes are suggested to have distinct lattice distortions and more exposed active sites (Du *et al.*, 2021; Nemani *et al.*, 2021).

Synthesis of MXenes With Different Surface Groups

Surface groups on MXenes are introduced spontaneously when the A layers are removed from MAX phases during the etching process. Hence, the etching conditions determine the terminating species of MXenes. For example, MXenes synthesized in the hydrofluoric acid (HF) solutions have a chemical formula $M_{n+1}X_n(OH)_xO_yF_z$ with mixed $-OH$, $=O$, and $-F$ surface groups; while NaOH etched MXenes are only terminated by $=O$ and $-OH$ and can be expressed as $M_{n+1}X_n(OH)_xO_y$ (Li *et al.*, 2018; Naguib *et al.*, 2014). To simplify the formula of MXenes, T_x is used to represent all surface groups.

First-principles calculations reveal that the work functions of MXenes strongly depend on the functional groups terminating the surface (Liu *et al.*, 2016). Simulations suggest that some of $=O$ terminated MXenes can spontaneously inject holes, and all the $-OH$ terminated MXenes can spontaneously transfer electrons (Je *et al.*, 2016). It has also been suggested that $-F$ groups can block the transport of ions and decrease the theoretical capacitance of MXene-based electrodes (Tang *et al.*, 2012). Based on whether the MXenes contain $-F$ surface groups or not, the synthesis methods of MXenes are classified into two general categories: Fluorine-based and non-Fluorine-based methods.

Fluorine Based Etching

HF is the earliest and the most commonly-used etchant to produce MXenes. A large variety of MXenes can be obtained by etching in 10%–50% HF solutions under proper reaction conditions (e.g., time and temperature). Taking the synthesis of $Ti_3C_2T_x$ MXene as an example, the reactions between the Ti_3AlC_2 MAX phase and HF can be described as:



Accordion-like multilayered MXenes are obtained after HF etching, and the layers of MXenes are held together by van der Waals interactions and hydrogen bonds (Naguib *et al.*, 2011).

However, handling HF solutions is dangerous because of its corrosive and hazardous nature. Mild etchants with mixed fluoride salt (LiF, NaF, NH_4F , FeF_3) and hydrochloric acid (HCl) are also effective for etching (Feng *et al.*, 2017; Halim *et al.*, 2014; Liu *et al.*, 2017; Wang *et al.*, 2017). Compared with the HF etching, the mild etchants contain cations (e.g., Li^+ , Na^+ , and NH_4^+) that can intercalate simultaneously into the interlayers of MXenes, leading to a more open layered structure. MXenes produced by the mild methods also show fewer defects and larger nanosheets than HF-etched MXenes, which increase the electrical conductivity of the MXene films (Ghidiu *et al.*, 2014). Additionally, more $=O$ and less $-F$ surface groups are observed on the LiF/HCl-etched MXenes than on the HF-etched MXenes, which may provide more active sites for surface redox reactions and increase the capacitance of the MXene-based electrode (Hope *et al.*, 2016).

Single- or few-layer MXenes are produced by mechanically exfoliating or chemically delaminating the multilayered MXenes. Applying the sonication or handshaking can easily separate the LiF/HCl-etched multilayered MXenes because the pre-intercalated Li^+ reduces the layer-to-layer interactions (Alhabeib *et al.*, 2017). Meanwhile, various organic molecules, such as dimethylsulfoxide (DMSO), N,N -dimethylformamide, and tetrabutylammonium hydroxide (TMAOH), must be added to weaken the interlayer coupling when delaminating the HF-etched multilayered MXenes (Mashtalir *et al.*, 2015; Mashtalir *et al.*, 2013; Naguib *et al.*, 2015). These organic molecules are difficult to remove, which negatively impacts the electrochemical performance of the MXene-based electrodes by reducing the conductivity and impeding ion transport.

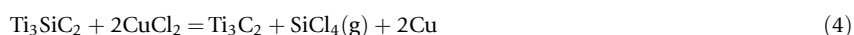
Non-Fluorine Based Etching

Alkali etching, electrochemical etching, iodine etching, and Lewis acid molten salt methods have been developed to synthesize MXenes without F surface groups. An alkali-assisted hydrothermal method uses a highly concentrated NaOH etchant to produce

–OH and =O terminated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (Li *et al.*, 2018). Meanwhile, electrochemical etching can exfoliate MAX phases in F-free acidic solutions. For example, the Ti_2AlC MAX phase can be electrochemically etched in HCl aqueous solution, forming Ti_2CT_x with –Cl, =O, and –OH surface groups (Pang *et al.*, 2019; Sun *et al.*, 2017). F-free Cr_2CT_x and V_2CT_x MXenes can also be obtained by electrochemically etching the MAX precursors in HCl at elevated temperatures (Pang *et al.*, 2019). In addition, electrochemical etching of Ti_3AlC_2 in non-acidic binary aqueous solution (1.0 M NH_4Cl and 0.2 M TMAOH) is possible due to the strong interaction between Cl^- and Al layers, producing $\text{Ti}_3\text{C}_2\text{T}_x$ with –Cl, =O, and –OH surface groups (Yang *et al.*, 2018b). A recent study reports an iodine etching method synthesizing F-free $\text{Ti}_3\text{C}_2\text{T}_x$ in the $\text{I}_2\text{-CH}_3\text{CN}$ mixture etchant. The iodine-etched $\text{Ti}_3\text{C}_2\text{T}_x$ is terminated with only =O and –OH groups because the Ti-I bond is so weak that it is spontaneously substituted by water or oxygen (Shi *et al.*, 2021).

MXenes with halogen-based functional groups have been synthesized by Lewis acid molten salt methods. Cl terminated MXene can be obtained from Al-MAX phases (MAX with Al A layers) through a replacement reaction and a subsequent exfoliation reaction in the ZnCl_2 molten salt (Li *et al.*, 2019b). Specifically, the Zn element from the ZnCl_2 molten salt replaces the Al element in Al-MAX, producing Zn-MAX; then, the Zn-MAX is exfoliated by the molten ZnCl_2 with strong Lewis acidity, forming Cl terminated MXene.

Molten CuCl_2 , FeCl_2 , NiCl_2 salts can all be used as reactants to synthesize MXenes from Al-MAX, Si-MAX, Zn-MAX, and Ga-MAX, if the redox potential of the molten salts is higher than that of the A elements in the MAX phases (Li *et al.*, 2020b). For example, the Si in Ti_3SiC_2 , which is difficult to be selectively etched by the traditional solution-based methods, can be removed by the molten CuCl_2 via:



The Cu^{2+} in the molten CuCl_2 can oxidize the Si to Si^{4+} because Cu^{2+}/Cu has a higher redox potential than Si^{4+}/Si at 700°C. Then, the Si^{4+} forms SiCl_4 gas, which escapes from the MXene sublayers (Li *et al.*, 2020b).

Tuning the Surface Groups by Post-Treatment

For $\text{M}_{n+1}\text{X}_n\text{T}_x$ MXenes with multiple types of surface groups, it is possible to tune the ratio between the surface groups by post-treatments, including chemical and thermal treatments. For example, the intercalation of hydrazine monohydrate reduces the number of –F and –OH surface groups on $\text{Ti}_3\text{C}_2\text{T}_x$ (Mashtalir *et al.*, 2016). Intercalating n-butyllithium into MXene can remove the –F groups while effectively introducing more =O groups (Chen *et al.*, 2019). Immersing multilayered MXene in basic aqueous solutions removes –F groups as the Ti-F bonds are unstable in solutions with high pH (Dall'Agnese *et al.*, 2014). Meanwhile, the ratio between different surface functional groups changes after heating MXenes in different atmospheres (Persson *et al.*, 2018; Rakhi *et al.*, 2015; Seredych *et al.*, 2019). Heating $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in helium leads to the desorption of H_2O and –OH species at lower temperatures, followed by the desorption of –F at higher temperatures (Seredych *et al.*, 2019). Removal of the –F groups can also be achieved by annealing MXenes in the N_2/H_2 (Rakhi *et al.*, 2015) or Ar/H_2 (Lai *et al.*, 2015) gas flows.

The $\text{M}_{n+1}\text{X}_n\text{Cl}_2$ and $\text{M}_{n+1}\text{X}_n\text{Br}_2$ MXenes obtained from the molten salt methods can be converted to MXenes with other surface groups by performing substitution and elimination reactions (Vladislav Kamysbayev, 2020). The $\text{Ti}_3\text{C}_2\text{Br}_2$ can react with Li_2Te , Li_2S , Li_2O , Li_2Se , and NaNH_2 in the CsBr-KBr-LiBr eutectic and yields –Te, –S, –O, –Se, and –NH terminated Ti_3C_2 , respectively. Furthermore, the exchange reaction between the Br-terminated MXene and LiH produces bare MXene without surface groups.

MXene-Based Electrodes in Aqueous Electrolytes

Charge Storage Process in Acidic Aqueous Electrolytes

Electrochemical methods, including cyclic voltammetry, galvanostatic charge and discharge (GCD), and electrochemical impedance spectroscopy (EIS), are used to speculate the charge storage mechanism of electrode materials. The shape of cyclic voltammogram (CV) and GCD curve can reflect the dominating charge storage mechanism. For example, a rectangular-shaped CV curve usually implies the EDL mechanism, whereas CV curves with well-separated peaks indicate battery-type behavior (Mathis *et al.*, 2019).

The CV curve of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrode in an acidic electrolyte shows peaks located at almost the same cathodic and anodic potential ($\Delta E_p \approx 0$, Fig. 2(a)), indicating a pseudocapacitive charge storage mechanism (Lukatskaya *et al.*, 2017; Mu *et al.*, 2019; Xu *et al.*, 2020). Plotting the logarithm of the peak current on the CV as a function of the logarithm of scan rate yields a curve with its slope called *b*-value (Forghani and Donne, 2018). The *b*-value of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes in an acidic electrolyte is close to 1, indicating that the surface-reaction mechanism dominates the charge storage process. EIS also gives an indication of capacitive or diffusion-controlled processes based on the slopes of the Nyquist plots at low frequencies. The Nyquist plot of $\text{Ti}_3\text{C}_2\text{T}_x$ electrode in acidic electrolytes is close to vertical at low frequencies, demonstrating capacitive behavior (Lukatskaya *et al.*, 2017).

While electrochemical methods are useful in evaluating the performance of MXenes as EES and provide information on the dominating charge storage mechanisms, more advanced characterization methods are used to obtain a detailed understanding of the process. In situ X-ray diffraction (XRD) was used to monitor the interlayer space change of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in H_2SO_4 aqueous

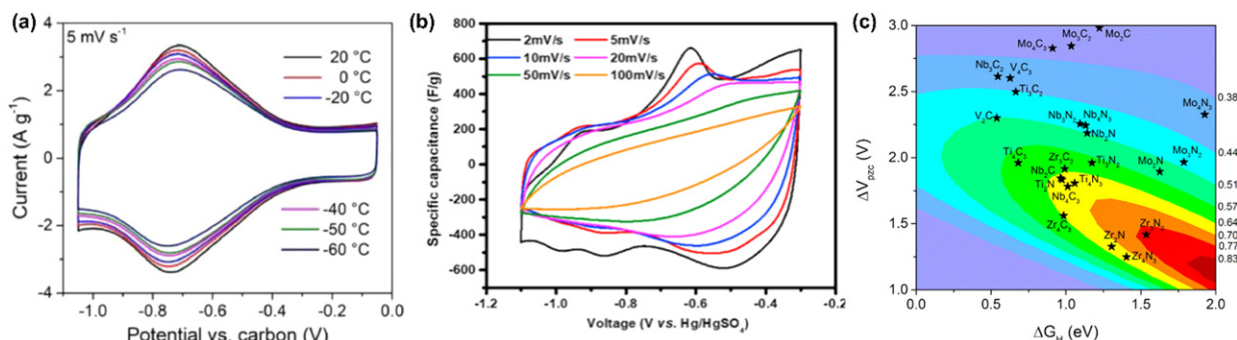
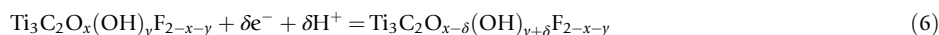


Fig. 2. (a) Cyclic voltammogram curve of $\text{Ti}_3\text{C}_2\text{T}_x$ in 1 M H_2SO_4 at different temperatures with a scan rate of 5 mV s^{-1} . Reproduced from Xu, J., Hu, X.H., Wang, X.H., et al., 2020. Low-temperature pseudocapacitive energy storage in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. *Energy Storage Materials* 33, 382–389, with copyright permission from Elsevier. (b) Cyclic voltammogram curve of V_2CT_x at different scan rates in 1 M H_2SO_4 at room temperature. Reproduced from Shan, Q., Mu, X., Alhabeb, M., et al., 2018. Two-dimensional vanadium carbide (V_2C) MXene as electrode for supercapacitors with aqueous electrolytes. *Electrochemistry Communications* 96, 103–107, with copyright permission from Elsevier. (c) Charge storage per formula unit versus the shift in the potential at the point of zero charge (ΔV_{PZC}) and hydrogen adsorption free energy (ΔG_{H}). Reproduced from Zhan, C., Sun, W., Kent, P.R.C., et al., 2019. Computational screening of MXene electrodes for pseudocapacitive energy storage. *The Journal of Physical Chemistry C* 123 (1), 315–321, with copyright permission from the American Chemical Society.

electrolyte based on the shift of the 002 XRD peak (Mu et al., 2019). The proton intercalation leads to a shrinkage of d -spacing of $\text{Ti}_3\text{C}_2\text{T}_x$ by $0.1 \text{ \AA}$ when the applied potential decreases from 0 to -0.6 V versus Ag. By further decreasing the applied potential to -0.9 V , the d -spacing rapidly expands by $0.5 \text{ \AA}$. The different trend of the d -spacing change with H^+ intercalation at different applied potentials is attributed to the change of the surface groups. Density functional theory (DFT) simulations revealed that the O-terminated Ti_3C_2 tends to shrink upon H^+ intercalation, whereas Ti_3C_2 with $-\text{OH}$ groups responds oppositely. More $-\text{OH}$ groups are formed as the intercalated protons are bonded with the $=\text{O}$ groups, leading to d -spacing expansion when the potential becomes more negative. The electrochemical reaction can be expressed as:



In situ X-ray absorption spectroscopy (XAS) measurements confirm the electrochemical reaction in $\text{Ti}_3\text{C}_2\text{T}_x$ when cycling in the acidic aqueous electrolyte (Lukatskaya et al., 2015). The shifts in the Ti K-edge energy were monitored to estimate the average oxidation state of the Ti at different applied potentials. The Ti valence decreases from $+2.43$ to $+2.34$ when the potential decreases from $+0.35$ to -0.35 V versus Ag/AgCl. The change of the Ti oxidation state corresponds to ~ 0.1 electron transfer per Ti in $\text{Ti}_3\text{C}_2\text{T}_x$ during the overall charging process. The electron transfer contributes a specific capacitance of 205 F g^{-1} , which is in good agreement with the experimental capacitance of 230 F g^{-1} .

As the total number of the transferred electron is smaller than 1, the electrochemical redox reaction in MXene is called the surface redox reaction. The surface redox reaction explains the high capacitance of the $\text{Ti}_3\text{C}_2\text{T}_x$ electrode in the acidic electrolyte despite its relatively low specific surface area ($20\text{--}100 \text{ m}^2 \text{ g}^{-1}$). Compared with the redox reaction, the surface redox is not diffusion-controlled and is almost unaffected as the temperature decreases (Fig. 2(a)) (Xu et al., 2020). DFT simulation was employed to describe the surface redox process theoretically (Zhan et al., 2018). It was found that the surface redox process dominates the overall charge storage process of $\text{Ti}_3\text{C}_2\text{T}_x$ in H_2SO_4 , but the EDL charge works against the surface redox process.

Charge Storage Process in Neutral Aqueous Electrolytes

Using less-corrosive non-acidic electrolytes solves the safety issue caused by the acidic electrolyte for portable and wearable EES applications. However, the capacitance of MXenes in the neutral aqueous electrolyte is much lower compared to that in the acidic electrolyte. For example, the volumetric capacitance of rolled multilayered $\text{Ti}_3\text{C}_2\text{T}_x$ clay electrode is 900 F cm^{-3} in 1 M H_2SO_4 (Ghidiu et al., 2014), and it is only 209 F cm^{-3} in 1 M Li_2SO_4 (Lukatskaya et al., 2013). The CV curves of MXene in the neutral aqueous electrolyte are almost rectangular-shaped without noticeable peaks, suggesting that the surface redox reactions (if any) are much weaker in the neutral aqueous electrolyte.

The weak oxidation and reduction of Ti in the neutral aqueous electrolyte are verified by the slight and reversible Ti K-edge energy shift when charging the Ti_2CT_x MXene in the Li_2SO_4 electrolyte. Molecular dynamics (MD) simulation was used to reveal the interfacial arrangement of the intercalated ions in MXenes (Gao et al., 2020a). The intercalated Li^+ , Na^+ , and K^+ tend to be closer to the electrode surface, and Cs^+ and Mg^{2+} are most likely to have a larger cation-surface distance. The simulation-estimated average cation-surface distance was found to have an inverse relationship with the capacitance of MXene in the neutral aqueous electrolyte.

Co-intercalation of water was observed in the Li^+ and Na^+ -based aqueous electrolytes by ex-situ XRD (Okubo et al., 2018). The intercalation of the highly hydrated Li^+ leads to the formation of EDL within the interlayer space of MXenes because the isolated atomic orbitals of the hydrated Li^+ cannot hybridize with the orbitals of the MXene (Ando et al., 2020). This explains the weakened

surface redox in the neutral aqueous electrolyte with lower capacitance. Notably, not all cation intercalations lead to the co-intercalation of water. Electrochemical quartz-crystal microbalance with dissipation monitoring (EQCM-D) measurements were used to reveal the $\text{Ti}_3\text{C}_2\text{T}_x$ electrode deformations during the cation intercalation process in neutral aqueous electrolyte. The result shows that highly charged small cations tend to contract the interlayer space of $\text{Ti}_3\text{C}_2\text{T}_x$ and larger cations with smaller charges expand the interlayer space (Levi *et al.*, 2015). Specifically, the water co-insertion occurs for Li^+ , Na^+ , Mg^{2+} , and Al^{3+} -based electrolytes, whereas water de-insertion happens for K^+ , Cs^+ , and tetraethylammonium ion (TEA^+) intercalation (Levi *et al.*, 2015).

Using water-in-salt (WIS) electrolyte has been reported to extend the negative potentials window of the MXene electrodes due to the suppressed hydrogen evolution (Kim *et al.*, 2019a,b). Meanwhile, the oxidation resistance of MXenes is also improved in the WIS electrolyte, which extends the positive potential window of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in the aqueous-based electrolytes from 0.1–0.2 V versus Ag/AgCl to 0.7–0.9 V versus Ag. The expansion of the positive potential window leads to a unique electrochemical process in the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in WIS electrolytes: a pair of strong and separated peaks emerge on the CV curves (Wang *et al.*, 2021). The electrochemical process is distinct from typical pseudocapacitive intercalation in MXenes because an abrupt reversible *d*-spacing change can be observed at the potential with peaks in CV. The abrupt *d*-spacing change is due to the co-insertion of 3 water per intercalated ion compared to the 1–1.5 water per intercalated ion for typical pseudocapacitive intercalations.

Capacitance of MXene-Based Electrodes

A hydrogel $\text{Ti}_3\text{C}_2\text{T}_x$ electrode demonstrated an exceptional volumetric capacitance up to 1500 F cm^{-3} in H_2SO_4 electrolyte with a significant contribution from surface redox reaction and high material density (Lukatskaya *et al.*, 2017). Other MXenes have also been investigated as electrodes for supercapacitors, showing promising performance. The lightest MXene, Ti_2CT_x , can deliver a high volumetric capacitance of 517 F cm^{-3} in 1 M KOH electrolyte (Zhu *et al.*, 2019). Compared with the Ti-based MXenes, Vanadium (V)-based MXenes are expected to have higher theoretical capacities due to the versatile oxidation state of V (V^{2+} , V^{3+} , V^{4+} , V^{5+}). Several peaks are present in the CV of V_2CT_x film in 1 M H_2SO_4 (Fig. 2(b)), suggesting a complicated redox process (Shan *et al.*, 2018). High specific capacitances of 487 F g^{-1} , 184 F g^{-1} , and 225 F g^{-1} were demonstrated for delaminated V_2CT_x film in 1 M H_2SO_4 , 1 M KOH, and 1 M MgSO_4 , respectively. However, the poor chemical stability of V in water prevents the practical application of V-based MXenes in aqueous electrolytes. $\text{Nb}_4\text{C}_3\text{T}_x$ film, which is more stable than Ti and V-based MXenes, has also demonstrated high volumetric capacitance of 1075, 687, and 506 F cm^{-3} in 1 M H_2SO_4 , 1 M KOH, and 1 M MgSO_4 , respectively (Zhao *et al.*, 2020). Many nitride members of the MXene family are predicted to have higher theoretical capacitance than carbide MXenes (Fig. 2(c)). More positive hydrogen adsorption energy and more minor shifts of the potentials at the potential of zero-charge of MXenes are considered the critical descriptors of higher capacitance (Zhan *et al.*, 2019).

As the surface redox reactions occur on the =O surface functional groups, the percentage of =O groups is crucial for the capacitance of MXenes. Meanwhile, the presence of –F groups is detrimental to the capacitance since they block the pathway of ion transport. Therefore, increasing the ratio of =O and decreasing the ratio of –F can potentially increase the capacitance of MXenes. The methods of tuning the surface groups have been discussed in Section “Synthesis of MXenes With Different Surface Groups”. For example, decreased content of –F groups is observed by simply immersing $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in KOH solution, which doubles the gravimetric capacitance ($\sim 300 \text{ F g}^{-1}$) of MXene in the H_2SO_4 electrolyte (Xie *et al.*, 2014). An even higher capacitance of 523 F g^{-1} in H_2SO_4 electrolyte was observed in the N-BuLi treated $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes as the –F is replaced by =O (Chen *et al.*, 2019). Notably, the maximum O terminations that $\text{Ti}_3\text{C}_2\text{T}_x$ MXene can take have been estimated to be $x = 3.5$ (Persson *et al.*, 2020). Further increasing the ratio of =O on the surface will break the structural integrity of $\text{Ti}_3\text{C}_2\text{T}_x$ and cause irreversible oxidation. Ti_3C_2 MXenes with –Cl, –Br, –I surface groups were investigated as cathodes for Zn^{2+} storage (Li *et al.*, 2021b). An exceptional electrochemical performance was achieved in halogen terminated MXenes since the surface groups participate in the redox reaction and contribute to extra capacity.

Heteroatoms doping, especially N-doping, can improve the electrochemical performance of MXenes since it increases the electrical conductivity and provides more redox-active sites. The most commonly used methods for N-doping are annealing MXenes in N-containing atmospheres or solutions (Tang *et al.*, 2017; Wen *et al.*, 2017; Yang *et al.*, 2017, 2018a). N-doped $\text{Ti}_3\text{C}_2\text{T}_x$ was prepared by annealing $\text{Ti}_3\text{C}_2\text{T}_x$ in ammonia, and the contents of N can be adjusted by tuning the annealing temperatures. The interlayer space of MXenes increases as the nitrogen atoms replace the carbon atoms in the X layers, which reduces ion transport resistance and increases capacitance (Wen *et al.*, 2017). MXenes also form composite electrodes with various nanomaterials, including polypyrrole, poly(3,4-ethylene dithiophene), polyaniline, MnO_2 , TiO_2 , Nb_2O_5 , CoS_2 , NiS, MoS_2 , and antimonene to increase the capacitance (Chandran *et al.*, 2020; Jiang *et al.*, 2018a; Li *et al.*, 2019a; Liu *et al.*, 2020a,b; Tong *et al.*, 2020; VahidMohammadi *et al.*, 2018; Yu *et al.*, 2019; Zhang *et al.*, 2016; Zhu *et al.*, 2016). In the composites electrodes, MXenes offer fast electron transport pathways and prevent the deformation of electrodes during cycling. Meanwhile, the other nanomaterials serve as pillars to prevent the restacking of MXenes and contribute extra capacity to the electrodes.

MXene-Based Supercapacitor in Non-Aqueous Electrolytes

Compared with the aqueous electrolytes, the applicable potential window of non-aqueous electrolytes is much broader, increasing the energy density of supercapacitors. The CV curves of MXene in the organic electrolytes also show pair of peaks on the anodic

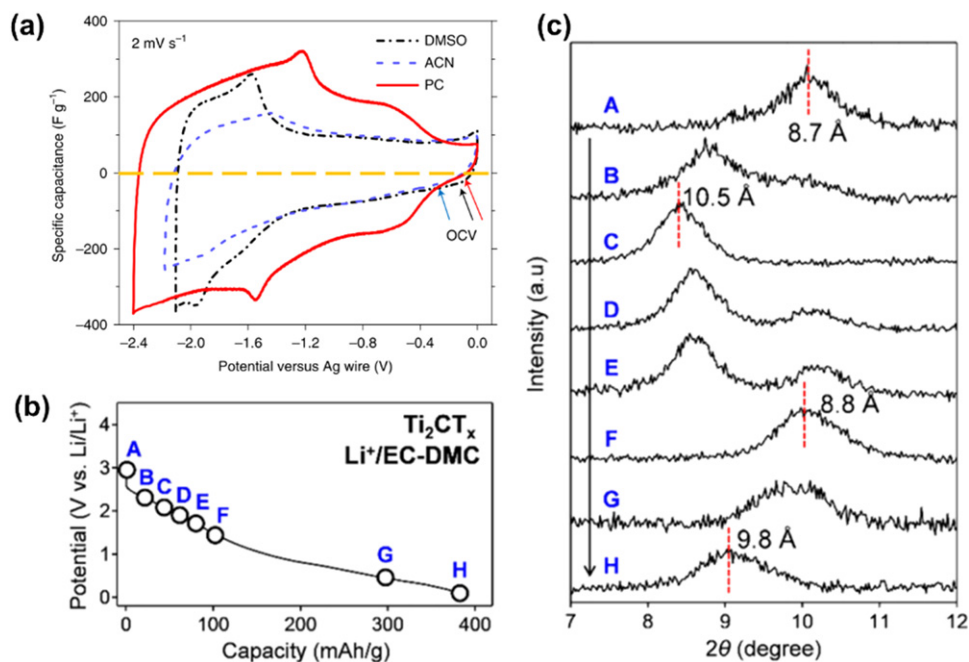


Fig. 3 (a) Cyclic voltammogram curve of macroporous $\text{Ti}_3\text{C}_2\text{T}_x$ with 1 M LiTFSI solvated in DMSO, ACN and PC organic electrolytes. Reproduced from Wang, X., Mathis, T.S., Li, K., et al., 2019. Influences from solvents on charge storage in titanium carbide MXenes. *Nature Energy* 4 (3), 241–248, with copyright permission from Springer Nature. (b) First charge curve at 20 mA g^{-1} for Ti_2CT_x in 1 M $\text{LiPF}_6/\text{EC-DMC}$ and (c) corresponding ex-situ X-ray diffraction patterns at different discharging states. Reproduced from Okubo, M., Sugahara, A., Kajiyama, S., Yamada, A., 2018. MXene as a charge storage host. *Accounts of Chemical Research* 51 (3), 591–599, with copyright permission from the American Chemical Society.

and cathodic branches with small ΔE_p , indicating a pseudocapacitive charge storage mechanism (an example is given in Fig. 3(a)). Ex-situ XAS of the Ti K-edge observed reversible reduction/oxidation of Ti in Ti_2CT_x when cycling in $\text{LiPF}_6/\text{ethylene carbonate (EC)-dimethyl carbonate (DMC)}$ electrolyte (Okubo et al., 2018). The position and intensity of the plasmon resonance peak of $\text{Ti}_3\text{C}_2\text{T}_x$ shift during cycling in Li^+ -based organic electrolytes, suggesting the change of Ti oxidation state (Li et al., 2021a). Hence, MXenes exhibit pseudocapacitive intercalation with surface redox reactions in the organic electrolytes.

The change of the d -spacing of MXene in respective to the applied potential depends on the type of surface groups. Small amplitude of the d -spacing change was observed when discharging the $\text{Ti}_3\text{C}_2\text{Cl}_2$ in the $\text{LiPF}_6/\text{EC-DMC}$ electrolyte (Li et al., 2020b). Meanwhile, the d -spacing of Ti_2CT_x electrode with randomly distributed surface groups expands and shrinks more significantly when potential decreases in the same organic electrolyte (Fig. 3(b-c)) (Okubo et al., 2018). Firstly, the d -spacing of 8.7 Å increases rapidly by about 1.8 Å when the potential drops from 3 V to 2 V versus Li/Li^+ , which can be correlated to the intercalation of solvated Li^+ . Then, the enlarged d -spacing of Ti_2CT_x disappears when the potential decreases from 2 V to ~ 1.5 V. Instead, a small d -spacing of 8.8 Å emerges due to the strong attraction between Li^+ and the MXene flakes, indicating the intercalation of desolvated Li^+ . When the potential becomes more negative, more Li^+ intercalate into the interlayer space and the interlayer space expands again.

The solvation level of the intercalated ion and the interfacial ion-solvent arrangement is correlated with the charge storage process of the MXene-based electrode and the charge storage capability. The atomic orbitals of the desolvated cations could overlap with the orbitals of MXenes and induce the redox reactions of MXene, giving rise to an intercalation pseudocapacitance through charge transfer from the ions to MXene sheets (Ando et al., 2020). This explains the strong redox peaks observed in CV when the intercalated Li^+ is fully desolvated in Lithium bis (trifluoromethanesulfonyl)imide (LiTFSI)-propylene carbonate (PC) electrolyte (Fig. 4a-c) (Wang et al., 2019). When DMSO is used as the solvent, two layers of DMSO molecules are present in the large interlayer space of MXene, forming an ion transport pathway with low resistance in-between the two layers of solvent molecules. By contrast, only one layer of acetonitrile (ACN) molecules are allowed in the MXene interlayers, which blocks the ion transport pathways. Hence, the specific charge (C g^{-1}) of $\text{Ti}_3\text{C}_2\text{T}_x$ increases in the sequence: in LiTFSI-ACN < in LiTFSI-DMSO < in LiTFSI-PC.

The Na^+ intercalation process of $\text{Ti}_3\text{C}_2\text{T}_x$ was explored in the $\text{NaPF}_6/\text{EC-DMC}$ organic electrolyte (Kajiyama et al., 2016). Solid-state ^{23}Na magic-angle spinning NMR observed the reversible intercalation and deintercalation of desolvated Na^+ (Fig. 4d). Some Na^+ ions are trapped in-between the interlayer space of $\text{Ti}_3\text{C}_2\text{T}_x$ during the first sodiation process. The remained Na^+ expands the interlayer space and assists in keeping the interlayer space of MXene constant during the Na^+ intercalation and deintercalation process, which improves the cycling stability and lowers the Na^+ intercalation resistance. The interlayer space change of V_2CT_x in the $\text{NaPF}_6/\text{EC-DMC}$ electrolyte was monitored by ex-situ XRD (Dall'Agnese et al., 2015). A continuous shift of the 002 peak from 9° to 12° was observed as the electrode potential increased from 1 to 3.5 V versus Na^+/Na , indicating a shrinkage of the interlayer space with desodiation.

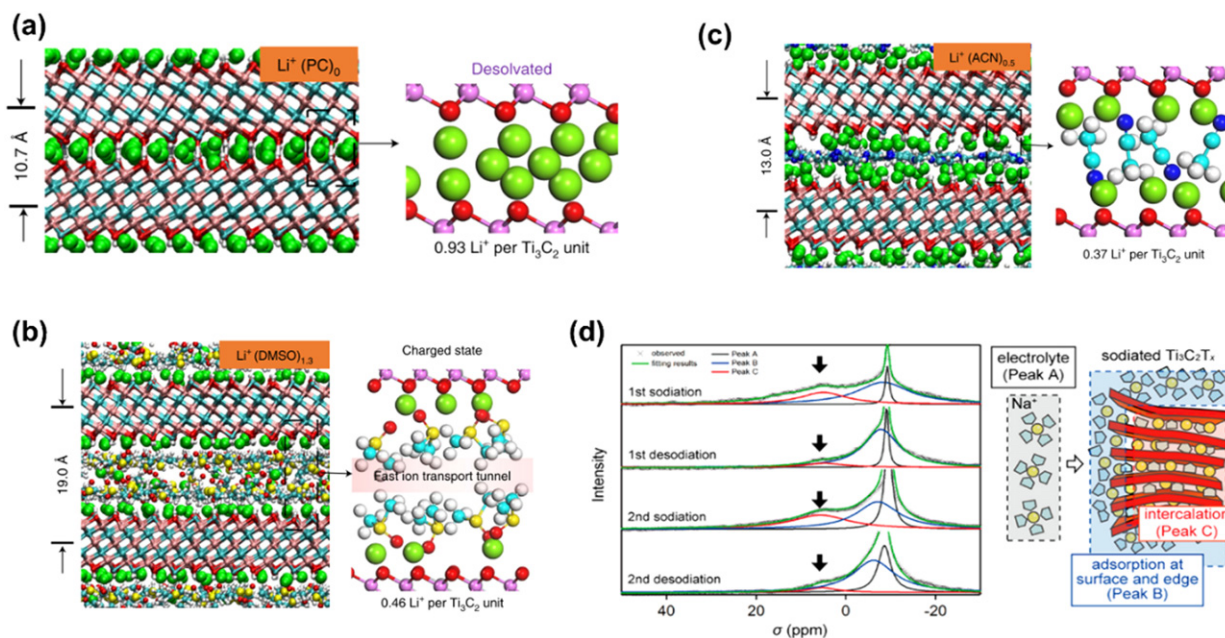


Fig. 4 (a)–(c) The molecular dynamics simulation and schematics of the local ion and solvent arrangements in macroporous $\text{Ti}_3\text{C}_2\text{T}_x$ with 1 M LiTFSI solvated in (a) PC (b) DMSO and (c) ACN. Reproduced from Wang, X., Mathis, T.S., Li, K., et al., 2019. Influences from solvents on charge storage in titanium carbide MXenes. *Nature Energy* 4 (3), 241–248, with copyright permission from Springer Nature. (d) Ex-situ solid-state ^{23}Na magic-angle spinning NMR spectra of the $\text{Ti}_3\text{C}_2\text{T}_x$ electrode during the initial two cycles in 1.0 M $\text{NaPF}_6/\text{EC-DEC}$. Reproduced from Kajiyama, S., Szabova, L., Sodeyama, K., et al., 2016. Sodium-ion intercalation mechanism in MXene nanosheets. *ACS Nano* 10 (3), 3334–3341, with copyright permission from the American Chemical Society.

A broad potential window can be applied to the MXene electrodes using ionic liquids (ILs) as electrolytes as the electrochemical stability of ILs is high. Using ILs electrolytes also dramatically improves the safety of the devices due to the high thermal stability, non-volatility, and non-flammability of ILs. (Wang et al., 2020) The charge storage process of MXenes in ILs was studied by monitoring the d -spacing change when cycling the $\text{Ti}_3\text{C}_2\text{T}_x$ in 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (EMIM-TFSI) (Lin et al., 2016b). The interlayer space of $\text{Ti}_3\text{C}_2\text{T}_x$ for EMIM^+ intercalation changes oppositely to that for TFSI $^-$ intercalation. The intercalation of EMIM^+ leads to the expansion of the interlayer space due to the steric effect of EMIM^+ . Meanwhile, the interlayer space shrinks when charging the electrode to a positive potential, which can be explained by the attraction between the intercalated TFSI $^-$ and the positively charged MXene surface.

Assisting the Ion Transport in MXenes

The weak van der Waal interactions between the 2D layers guarantee good electrolyte ion accessibility for the thin-film electrodes filtered from the delaminated MXene colloidal solutions (Fig. 5a). Restacking issue of the MXene layers occurs when the thickness of the electrode increases, which impedes the ion intercalation and lowers capacitance, especially at high rates (Wang and Bannenberg, 2021). For instance, a 75 μm -thick- $\text{Ti}_3\text{C}_2\text{T}_x$ film can only deliver a specific capacitance less than half of that of 5 μm -thick- $\text{Ti}_3\text{C}_2\text{T}_x$ film in H_2SO_4 at 2 mV s^{-1} , and becomes less than a quarter at 100 mV s^{-1} (Ghidiu et al., 2014). Larger cations are more difficult to intercalate deeply into the MXene layers, suggesting that the restacking issue impairs the performance more significantly in the neutral aqueous electrolyte (Chen et al., 2021).

Introducing Spacers in the Interlayers

Preintercalating ions or low-dimensional (1D or 2D) materials can effectively restrain the restacking of MXene flakes. Pre-intercalation of alkali ions enlarges the interlayer space of $\text{Ti}_3\text{C}_2\text{T}_x$ and increases the capacitance in the H_2SO_4 electrolyte (Li et al., 2017a). Increasing the size of the preintercalated ions leads to larger interlayer space and more apparent increases in the capacitance of MXene. Similarly, the Na-intercalated V_2CT_x shows increased volumetric capacitance, even surpassing that of $\text{Ti}_3\text{C}_2\text{T}_x$ in various electrolytes, including H_2SO_4 , ZnSO_4 , K_2SO_4 , and MgSO_4 aqueous electrolytes (VahidMohammadi et al., 2019). Pre-intercalation is essential for the performance of MXene-based electrode when using ILs electrolytes (Lin et al., 2016a). The pure $\text{Ti}_3\text{C}_2\text{T}_x$ electrode shows an extremely low capacitance of 1 F g^{-1} in EMIMTFSI electrolyte. Pre-intercalating EMIMTFSI IL effectively increases the capacitance of $\text{Ti}_3\text{C}_2\text{T}_x$ to 70 F g^{-1} .

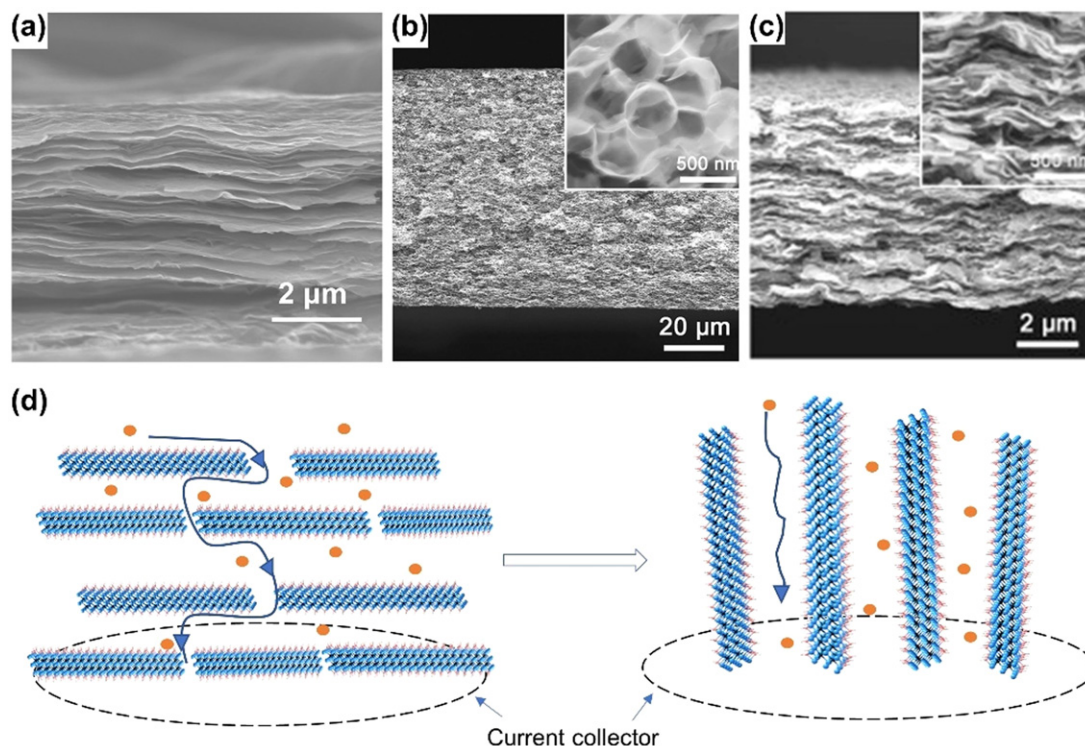


Fig. 5 Cross-sectional SEM images of (a) $\text{Ti}_3\text{C}_2\text{T}_x$ filtered film, (b) 3D macroporous $\text{Ti}_3\text{C}_2\text{T}_x$ film, and (c) wavy $\text{Ti}_3\text{C}_2\text{T}_x$ film. **Figs. 5b** and **5c** are reproduced from Ref. Li, K., Wang, X.H., Wang, X.F., et al., 2020a. All-pseudocapacitive asymmetric MXene-carbon-conducting polymer supercapacitors. *Nano Energy* 75, 104971, with copyright permission from Elsevier. (d) A schematic shows the ion transport pathways (illustrated as arrows) in horizontally aligned and vertically aligned $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films.

1D carbon nanotubes (CNT) were sandwiched in-between $\text{Ti}_3\text{C}_2\text{T}_x$ layers by an alternating filtration method (Zhao et al., 2015). The capacitance retention is 74% at 200 mV s^{-1} for $\text{Ti}_3\text{C}_2\text{T}_x$ with CNT in 1 M MgSO_4 , and is only 45% for pure $\text{Ti}_3\text{C}_2\text{T}_x$. Ion accessibility is also greatly improved for organic electrolytes when CNT is introduced to MXene interlayers (Liu et al., 2015). $\text{Ti}_3\text{C}_2\text{T}_x$ -CNT composite electrode exhibits high capacitance retention in the organic electrolyte at a scan rate of 10 mV s^{-1} , even at a low temperature of -60°C (Gao et al., 2020b). 2D materials can also function as spacers to prevent the restacking of MXene and increase the interlayer space. MXene/reduced graphene oxide (rGO) film prepared by self-assembly demonstrated a high volumetric capacitance of 1040 F cm^{-3} in 3 M H_2SO_4 at 2 mV s^{-1} , and an impressive rate capability with 61% capacitance retention at 1 V s^{-1} (Yan et al., 2017). Stacking MXenes with other 2D materials provides interlayers with asymmetric interactions from two surfaces, which may construct an electrode that combines the advantage of two individual 2D materials and eliminate the associated shortcomings (Pomerantseva and Gogotsi, 2017).

Building 3D Architecture

Another strategy to alleviate the restacking of MXenes and facilitate ion transport is to construct unique MXene architectures, such as 3D macroporous structure, wavy structure, and vertically aligned MXenes. Macropores can be introduced in MXenes by polymer-templated methods that the polymer templates are first filtrated with MXene flakes and then are removed by annealing (Fig. 5b) (Lukatskaya et al., 2017; Zhao et al., 2017). Ice templates, which are formed from the interfacial water during the freeze-drying process, are also capable of generating pores in MXene-based electrodes (Zhang et al., 2020b). Constructing MXene electrodes with 3D macroporous structures shortens the ion transport distance by forming electrolyte reservoirs in the electrodes, which are especially beneficial for high-rate operations in thick-film electrodes. A $13 \mu\text{m}$ -thick-macroporous $\text{Ti}_3\text{C}_2\text{T}_x$ film showed high capacitance at ultrahigh scan rates: 210 F g^{-1} at 10 V s^{-1} and 100 F g^{-1} at 40 V s^{-1} (Lukatskaya et al., 2017). When the thickness of the macroporous MXene increases to $180 \mu\text{m}$, a high capacitance of 125 F g^{-1} can still be obtained at 1 V s^{-1} . However, introducing macropores inevitably reduces the packing density of MXene film electrodes and decreases the volumetric capacitance. Compressing the polymer-templated macroporous MXenes forms a wavy structure (Fig. 5c), which offers good ion accessibility with significantly increased packing density. The wavy MXenes with a high mass loading of 2.28 mg cm^{-2} demonstrated high volumetric capacitance of 1136 F cm^{-3} (299 F g^{-1}) at 1000 mV s^{-1} and 790 F cm^{-3} (208 F g^{-1}) at 5000 mV s^{-1} (Li et al., 2020a).

When the balance between the electrostatic repulsion force and the Van der Waals interactions between 2D layers are disrupted by gelation agents, MXenes flakes will interconnect and assemble into 3D porous architectures (Jiang et al., 2018b; Li et al., 2017b;

Shang *et al.*, 2019; Zhang *et al.*, 2018; Zhao *et al.*, 2018b). The addition of a weak reducing agent, ethylenediamine (EDA), can initiate the assembly of MXene flakes into 3D networks and form $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel electrodes (Li *et al.*, 2017b). Adding graphene oxide as a crosslinking agent assists the construction of the 3D macrostructure of MXene hydrogel (Shang *et al.*, 2019). A wrinkled $\text{Ti}_3\text{C}_2\text{T}_x/\text{rGO}$ hydrogel delivered a high gravimetric capacitance of 370 F g^{-1} at 5 A g^{-1} and 165 F g^{-1} at 1000 A g^{-1} in H_2SO_4 electrolyte.

Assembling MXene electrodes with vertical alignment on the current collectors offers a solution to the restacking issue caused by large electrode thickness. The vertical alignment of MXene flakes was first prepared by mechanical shearing of a discotic lamellar liquid-crystal phase of $\text{Ti}_3\text{C}_2\text{T}_x$ with an assist from a non-ionic surfactant (Xia *et al.*, 2018). The capacitance of the MXene-based electrode is thickness-independent up to an electrode thickness of $320 \mu\text{m}$. The ion diffusion distance becomes much shorter with the vertically aligned structure than that of the horizontally stacked flakes (Fig. 5d). In addition, the direction of ion transport is parallel to that of the electric field, which benefits ion acceleration. Hence, vertically aligned MXene electrodes show excellent high-rate performance regardless of the electrode thickness or mass loading. For example, the rate capability of a $320 \mu\text{m}$ -thick electrode is almost the same as a $40 \mu\text{m}$ -thick electrode at 100 V s^{-1} . Furthermore, instead of adding surfactants or binders, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene can form a nematic liquid crystal phase by simply tuning the concentration of the MXenes colloidal solutions (Zhang *et al.*, 2020a). Fiber electrodes that are fabricated from the pure liquid-crystal MXene delivered a high volumetric capacitance of 1265 F cm^{-3} in $1 \text{ M H}_2\text{SO}_4$.

Generating Pinholes on Flakes

Creating pinholes on MXenes flakes shortens the ion diffusion distance by generating new ion transport pathways. Post-etching $\text{Ti}_3\text{C}_2\text{T}_x$ with concentrated H_2SO_4 introduces holes on the flakes and enlarges the interlayer space. Capacitance retention of 39.0% was achieved on the H_2SO_4 post-treated $\text{Ti}_3\text{C}_2\text{T}_x$ as the scan rate increases from 5 mV s^{-1} to $10,000 \text{ mV s}^{-1}$ (Tang *et al.*, 2020). Porous $\text{Ti}_3\text{C}_2\text{T}_x$ can also be prepared by chemical etching MXene in aqueous solutions of transition metal salts (e.g., CuSO_4 , CoSO_4 , FeSO_4) followed by acid treatments (Ren *et al.*, 2016). Additionally, partially electrochemical oxidation of MXene in the acidic electrolyte can also open holes on MXene flakes and increase the high-rate performance (Tang *et al.*, 2019). Notably, the electrochemical oxidation potential should be lower than 0.3 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ to avoid the irreversible formation of TiO_2 . Furthermore, corrosive alkali post-treatment of the multilayered MXenes increases the high-rate performance as the treatment crumples MXene flakes, generates holes, and simultaneously preintercalates alkali ions (Ming *et al.*, 2019; Zhao *et al.*, 2018a).

Conclusion

This article overviews the ion intercalation process in MXene-based pseudocapacitor with various electrolytes. Titanium-based MXenes deliver high volumetric capacitance and rate capability in the acidic aqueous electrolyte due to the fast surface redox reactions between the intercalated proton and surface groups. We discuss the influential factors for the performance of MXene-based electrodes in the aqueous electrolytes and briefly summarize the strategies to increase the capacitance. We also show that the ion intercalation process in MXene with non-aqueous electrolyte is different from the aqueous electrolyte in terms of the change of interlayer space, intercalated species, and the interfacial ion-solvent arrangement. Furthermore, the poor ion accessibility caused by the restacking of the 2D layers leads to considerable ion intercalation resistance, which is detrimental to the capacitance and the high-rate performance of MXene-based electrodes in all types of electrolytes. Hence, we summarize the strategies to increase ion accessibility, including inducing spacers, building 3D architecture, and generating holes on MXene flakes.

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Battery Carbons

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Abstract

The high electrical conductivity and electrochemical stability of carbon material made it an inevitable material in battery applications. The application of carbon to batteries increases tremendously with the development of lithium ion batteries. The surface area of the carbon material can be reducing by processing which leads to low irreversible losses and high reversible capacity in batteries. In this chapter, the methods for reducing the surface area of carbon are discussed in brief. Also, the process of intercalation of lithium into graphite, soft carbon, hard carbon and doped carbon and its effects are elaborated. Graphite with high rhombohedral phase prevents the exfoliation of graphite when intercalated with lithium.

Key Points

- Brief overview of carbon based lithium-ion batteries.
- Specific Energy and Reversibility property of carbon electrode in lithium-ion batteries.
- Intercalation of lithium in Graphite and its irreversible and reversible capacity.
- Intercalation of lithium in soft carbon exhibits two domains of electrochemical behavior according to heat treatment temperature.
- Intercalation of lithium in hard carbon and its influence on irreversible and reversible capacity.
- Intercalation of lithium in doped carbon to reduce irreversible losses.

Introduction

From the very beginning of battery manufacturing in the second half of the nineteenth century, carbon materials have proved to be very useful as constituents of many systems because of their high electrical conductivity and their relative electrochemical stability. Although thermodynamics indicates a restricted domain of carbon stability in potential–pH diagrams, oxidation and reduction reactions do not generally occur under normal conditions of temperature and pressure. Thus, carbon rods have been used, and are still used, as current collectors in Leclanché Zn/MnO₂ cells. As oxides and hydroxides, used as the cathode of many types of battery, are not good electronic conductors, they have to be mixed with a conducting powder. For this purpose, graphite and carbon blacks have found universal application. For example, nickel hydroxide (in some alkaline secondary batteries) and mercuric oxide (in Mallory primary batteries) are mixed with 10–20% by weight of graphite flakes. In manganese dioxide, cathodes of Leclanché cells, certain carbon blacks, such as acetylene black, are preferred, because their chain-like structure (the so-called ‘primary structure’) gives them a high absorptive power for electrolyte, in addition to conductivity enhancement. In zinc/air primary batteries, derived from the zinc/manganese dioxide cell, the central MnO₂/carbon black paste is replaced by a gas diffusion electrode in the form of a cylinder of porous activated carbon connected to an external air supply through its top surface. Porous carbons or carbon felts are also used as current collectors in Li/SOCl₂ primary batteries or as supports for noble metal catalysts in fuel cells.

These few examples show that the field of carbon application to batteries is broad. In addition, it has expanded tremendously with the development of the so-called lithium ion batteries which will constitute the main topic of this article. Lithium metal combines the lowest standard potential (–3.045 V vs. NHE) with a low atomic weight ($M/4$ 6.94) to give an exceptionally high theoretical specific capacity of 3860 mAh g^{–1}. In combination with a cathode material, generally a transition metal oxide, and using a suitable nonaqueous electrolyte, battery voltages of about 4 V are obtained. Primary lithium batteries have been fabricated on this basis and commercialized since the end of the 1960 s. However, the development of rechargeable lithium batteries was prevented because of the problem of dendrite formation during charging, resulting in poor cycling efficiency and cell shorting. The problem was solved in 1990 when Sony announced the commercialization of lithium ion batteries, where lithium metal is replaced by a carbon host structure that can reversibly absorb and release lithium ions at low electrochemical potentials.

The smart solution of electrode morphology stabilization by using a host structure makes these batteries belong to the so-called ‘rocking-chair’ battery family, where ions spontaneously exchange from one intercalation structure to another. In the case of carbon-based lithium ion batteries, the lithiated carbon is a powerful reducing agent (negative electrode) whereas a metal oxide constitutes the positive electrode. This concept was proposed as early as 1980 by [Armand *et al.* \(1980\)](#). At that time, carbons were known to intercalate lithium by a chemical route, the maximum amount being achieved with graphite (LiC₆), but early attempts to use graphite as a negative host structure in lithium ion batteries failed because of strong reactivity with the electrolyte. Other less

crystalline materials (heat-treated cokes) were found to be less sensitive to the electrolyte, but presented still modest performances. Then, highly disordered materials (non-graphitizing carbons and low-temperature carbons) were shown to exhibit different electrochemical behavior due to their differences in structure, texture, and heteroatom content. Finally, crystalline materials regained interest when it was demonstrated that they could be used in electrolytes with suitable solvent composition, mainly based on ethylene carbonate (EC).

Main Properties of Carbon Electrodes

Specific Energy

The replacement of metallic lithium by a lithiated carbon results in a decrease in energy density because of the presence of the host structure. The basic requirement is the highest possible amount of lithium ions reversibly intercalated into the carbon matrix at a potential close to that of metallic lithium. This property depends on the carbon host structure. Owing to the importance of this subject for this article, it will be presented in Sections 3–6 with separate treatment of the main carbon families.

Reversibility

All carbon materials experience irreversible side reactions during the first electrochemical absorption of lithium ions. These reactions consume lithium and have to be minimized, since they lead to a capacity loss (the so-called ‘irreversible capacity’). A well-known source of irreversibility is electrolyte instability at low potential, which yields insoluble products. No electrolyte has been found that withstands the low electrochemical potential of metallic lithium or lithiated carbons. As the potential of the negative electrode lowers, the electrolyte is reduced until the formation of an electronically insulating (passivating) layer on the carbon particles, often called SEI (solid electrolyte interphase), allows further lithium exchange. This process is clearly visible on the galvanostatic curves as an irreversible plateau at a potential close to 0.8 V versus Li^+/Li (Fig. 1). A major contribution to the knowledge of the layer composition and electrolyte reduction mechanism came from the work of Aurbach and coworkers (Aurbach *et al.*, 1997). They showed that cyclic carbonates like propylene carbonate (PC) or ethylene carbonate (EC) are the best suited solvents, as they yield double lithium alkyl carbonates with a good passivating ability.

A direct way to minimize the irreversible capacity associated with the formation of the passivating layer is to decrease the exchange surface area. As the use of carbon powders is mandatory to increase the kinetics of lithium exchange to an acceptable level, a compromise solution is a specific surface area of a few square meters per gram with particle sizes of a few micrometers. For this purpose, materials with a special particle morphology, such as carbon spheres grown from mesophase or carbon fibers, can be attractive. However, as shown in Sections 3–6, other sources of irreversible losses in the first cycle can exist, such as exfoliation or lithium reaction with heteroatoms and structural defects. Obviously, they depend on the structure, texture, and composition of the carbon.

The irreversible capacity loss due to formation of passivation layer on the surface of carbon can be minimized by reducing the surface area. The surface area is minimum for spherical shape and the conversion of irregular shape to spherical shape is possible by simple preparation method. The phenolic resin and methylnaphthalene-derived mesophase pitch (MNMP) powders are employed as the precursor for hard carbon and graphite, respectively. The irregular-shaped precursor powders are converted to spherical carbons by first coating with fine-grained fumed silica powder with hydrophobic surface and carbonizing/graphitizing under an argon atmosphere. The conversion takes place near glass transition temperature of the resin for carbon and softening point of the pitch for graphite. The spherical hard carbon has higher tap density, hence large amount of negative electrode material can be loaded to achieve high volumetric energy density (Ou Jung *et al.*, 2004).

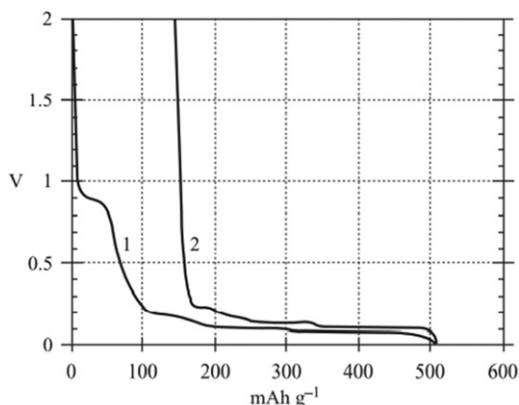


Fig. 1 First discharge (1) and charge (2) curves of a lithium/natural graphite cell. The plateau at 0.8–0.9 V on the discharge curve is characteristic of passivating layer formation. The other plateaus at potentials below 0.3 V are signatures of transitions between different stages (see Section “Reversible Capacity and Phase Diagram”).

A LiFePO_4 nanoparticles combining the disordered microporous carbon AC-K5 prepared by impregnation from ethanol solution of the LiFePO_4 precursors has continuous porous carbon network with high surface area. The size and morphology of the porous carbon supported LiFePO_4 nanoparticles depended strongly on the LiFePO_4 loading amounts. Lower loading amount of LiFePO_4 resulted in more homogeneous dispersion of particles with narrower size distribution, high-rate performance, and discharge capacity of 66 mAh g^{-1} at 50°C (Min and Qiuming, 2011).

Lithium Intercalation Into Graphite's

Irreversible Capacity and Exfoliation

Highly crystalline carbons often exhibit a large irreversible capacity regardless of their surface area. This occurs especially with PC-containing electrolytes and results from exfoliation of graphene layers. In this case, before the complete formation of the passivating layer, solvated lithium ions are intercalated. Further reduction causes the decomposition of the solvent molecules between the graphene layers, with production of gaseous compounds like propylene which exfoliate the graphite matrix. The newly created surface area then needs extra passivation, resulting in a dramatic increase in the irreversible capacity (from a few tens up to 1000 mAh g^{-1} of carbon in some cases).

As crystalline materials are highly desirable to achieve high energy densities, improvement of their electrochemical behavior has been the subject of many studies. It has been shown (Ohzuku *et al.*, 1993; Besenhard *et al.*, 1995) that solvent co-intercalation, and thus exfoliation, does not generally occur in EC-based electrolytes. The difference in behavior of such close molecules as EC and PC is not fully understood as yet. However, the beneficial effect of EC against exfoliation is not observed for all graphite's.

A better way to prevent exfoliation is the use of graphite grades with a high percentage of rhombohedral phase. The most common structure of graphite is the hexagonal Bernal structure, where the carbon layers are arranged in the ...ABAB... sequence with a shift of the B layers with respect to the A layers. Another crystalline form of graphite, thermodynamically metastable, can exist with a rhombohedral structure of ...ABCABC... stacking sequence. This form is never pure. It is always mixed with the hexagonal form in variable amounts, which can be increased up to 30%–40% of rhombohedral phase by a mechanical treatment. Such as grinding. Although graphite's with different rhombohedral phase content are indistinguishable in terms of reversible lithium capacity, it is not the same for the irreversible capacity, as shown by Simon *et al.* (1998). When the rhombohedral phase content is higher than 30% graphite exfoliation does not occur, even with electrolytes containing a high percentage of PC, a solvent otherwise interesting for its physical properties. From Raman spectroscopy experiments it has been shown that structure defects, localized at grain boundaries between rhombohedral and hexagonal domains, hinder the layer opening necessary for the intercalation of bulky solvated lithium ions.

Reversible Capacity and Phase Diagram

In the conditions where unsolvated lithium ions are electrochemically intercalated into graphite, and once the passivating layer has been formed, reversible intercalation of lithium takes place. The theoretical capacity of 372 mAh g^{-1} (LiC_6) is generally approached if the charge–discharge regime is slow enough (rate typically lower than $\text{C}/20$, where C is the capacity of the cell). The potential curves exhibit several reversible plateaus in the range 0–0.25 V versus Li^+/Li . As is well known, the existence of potential plateaus corresponds to transitions between different single phases and the end points of the plateaus give the composition range of biphasic domains. In the case of graphite intercalation compounds (GICs), the single phases are obviously compounds of defined stage. Indeed, one of the most important characteristics of GICs is the staging phenomenon, which corresponds to a periodical arrangement of intercalated layers within the graphite layer matrix. GICs are thus classified by a stage index denoting the number of graphite layers that separate two successive intercalated layers. The electrochemical lithium–carbon phase diagram has been determined using *ex situ* or in situ X-ray diffraction and Raman spectroscopy. Analysis of the data leads to the following conclusions. Transitions between stage 1 (LiC_6) and stage 2 (LiC_{12}), stage 2 and a dilute lattice-gas disordered stage 2 called stage 2 L (LiC_{18}), stage 2 L and stage 3, and stage 4 and a dilute stage 1 occur at about 0.09, 0.12, 0.14, and 0.20 V, respectively. The compositions of stage 3 and stage 4 compounds are not always well defined. In addition, the transition between these two stages seems to be continuous with a progressive variation of the cell voltage, which is not understood as yet. For low lithium content, the intercalated lithium is randomly distributed throughout the graphite host in a dilute stage 1 phase.

Lithium Intercalation Into Graphitizable Carbons

Graphitizable (“soft”) carbons are carbon materials whose structure evolves progressively toward the graphite structure when they are heat treated at high temperatures, up to 3000°C . They are composed of more or less misoriented crystallites whose size and crystalline order increase with the heat-treatment temperature (HTT). At the beginning of the graphitization step (HTTE1200– 1300°C), the size of the crystallites is of the order of 5 nm, both parallel and perpendicular to the layers (L_a and L_c , respectively), with an average interplanar distance d_{002} close to 0.344 nm. The crystallite size is about 10 nm at HTTE2000 $^\circ\text{C}$ and reaches several tens of nanometers with higher HTTs, while d_{002} approaches the graphite value (0.3354 nm). Typical soft carbons are graphitizable cokes, ex-mesophase fibers, vapor-grown fibers, or mesocarbon microbeads (MCMB).

All these materials, heat treated in the temperature domain where graphitization occurs (1300–3000 °C), exhibit common features for lithium electrochemical intercalation. First, the irreversible losses in the first cycle decrease with HTT, except at the end of the graphitization process. This is a consequence of a decrease in active surface area resulting from the structural reorganization (elimination of microporosity). As expected, the effect is more important at the beginning of the graphitization process (HTTE1300–2000 °C). In highly graphitized samples (HTTE2800 °C and above), some exfoliation occurs, as in graphite, producing an increase in the irreversible losses. Second, the reversible capacity values are lower than for graphite and exhibit a minimum for samples treated at about 2000 °C. In addition, this HTT value delimits two domains with different potential behaviors. For soft carbons heat treated above this temperature, the cell voltage exhibits the progressive appearance of plateaus characteristic of diphasic domains, whereas for carbons heat treated at 2000 °C and below, the potential varies continuously, as expected for monophasic systems.

Thus, the results point to the existence of two domains of electrochemical behavior according to whether the heat-treatment temperature is higher or lower than 2000 °C. In fact, it is well known that this value of HTT is a critical value in the graphitization process. It corresponds to the beginning of the three-dimensional ordering, which is evidenced by the appearance of modulations on the (hk) bands of the X-ray spectra. The increase of reversible capacities at HTTs above 2000 °C can therefore be understood as resulting from increased crystallinity. On the other hand, the capacity increase for lower HTTs is unexpected. Several explanations have been proposed, based on Franklin's or Mering's graphitization models (Flandrois and Simon, 1999). Nano $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /multiwalled Carbon Nano Tube (CNT) composite is prepared by liquid deposition technique has particle size of 100 nm is homogeneously dispersed in carbon matrixes. This composite is used as anode materials for lithium-ion batteries exhibits high performance electrochemical properties. This composite has lower polarization, excellent cyclic stability, and good rate capability compared to the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. At the discharge current density of 875 mA g^{-1} , the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT composite with 10 wt% carbon has the discharge capacities of 138.6 mAh g^{-1} . It maintained high-capacity retention of 99% after 100 cycles (Tingting *et al.*, 2015).

Lithium Insertion Into Low-Temperature Carbons and Non-Graphitizing Carbons

The pyrolytic conversion of organic compounds to carbon residues at temperatures below 1000 °C occurs by a complex chemistry, which involves a great number of parallel and sequential reactions and depends on the nature of the starting materials. Nevertheless, after the primary step of carbonization (up to 500–600 °C), all carbonaceous materials are made up of similar elemental bricks with different relative arrangements (Oberlin and Throuer, 1989). The elemental unit, or basic structural unit (BSU), contains planar aromatic structures consisting of about 10–20 rings, which are piled up more or less parallel in groups of two to four. In the case of soft carbons, by increasing HTT the BSUs form distorted columns which coalesce during the graphitization step. In non-graphitizing ("hard") carbons, the presence of cross-linking groups, especially when the precursor contains oxygen, hinders the formation of columns and their coalescence. Whatever the graphitization degree they can reach, carbonaceous materials heat treated between 500 and 1000 °C exhibit common features: low crystallinity, large amount of micro- or nano porosity, and presence of heteroatoms left from the organic precursor, essentially hydrogen, nitrogen, oxygen, and sulfur, depending on the precursor.

Whereas it is justifiable to talk about lithium 'intercalation' in the case of soft carbons during the graphitization step (i.e., lithium introduction into the interspace of carbon layers), in the case of hard carbons and low-temperature carbons where the BSU size is 1–1.5 nm, the lithium storage cannot be restricted to the interspace between aromatic molecules. Clearly, the low crystallinity, the internal porosity, and the presence of heteroatoms and functional groups have a strong influence on the reversible and irreversible capacities. The electrochemical behavior of a large number of carbonaceous materials pyrolyzed at temperatures between 500 and 1100 °C has been investigated. The main features are: (1) high reversible capacities, which can be more than twice the value of graphite; (2) high irreversible capacities in the first cycle (up to several 100 mAh g^{-1}); and (3) large hysteresis in the potential curves, i.e., lithium ions are inserted near 0 V and removed at about 1 V. The hysteresis in the potential profile has been correlated to the residual hydrogen content (Tao *et al.*, 1996). Heat treatments above 1000 °C eliminate hydrogen from the carbon, but the reversible capacity also decreases. Some hard carbons heat treated between 1000 and 1200 °C can maintain reversible capacities higher than 400 mAh g^{-1} . In addition, they develop a pronounced low potential plateau (below 0.1 V) and little hysteresis. If their irreversible capacity could be reduced, as it has been done, for example, through the chemical vapor deposition (CVD) of a carbonaceous layer on the surface of a carbon prepared from sucrose (Buiel and Dahn, 1998), such carbon materials would be of great interest.

LiFePO_4 is an ideal cathode material for lithium-ion batteries due to its high energy density, good thermal and chemical stability, and high-capacity retention. The electronic conductivity and lithium diffusion coefficient are very poor at room temperature. The conductivity can be improved by decreasing the particle size to nanoscale and to ensure good contact of the electrode materials, mesoporous LiFePO_4 positive electrodes were developed. Mesoporous LiFePO_4 are prepared by a one-pot reaction using hydrophilic carbon nanoparticles (20–30 nm) as the template exhibits a high discharge capacity of 137 mAh g^{-1} at 1 °C. After high-rate charge and discharge at 30 °C (one full discharge in 2 min) its capacity can be recovered to 160 mAh g^{-1} (Ren and Bruce, 2012).

Lithium Intercalation Into Doped Carbons

Carbons, and especially low-temperature carbons, are not pure carbon. They usually contain from a few parts per million up to a few percent of foreign atoms. However, it is possible to introduce foreign atoms into the carbon lattice intentionally, a process known as doping. Doping methods include: (1) co-deposition by CVD of carbon and foreign atoms (e.g., boron, nitrogen), (2)

pyrolysis of organic molecules containing foreign atoms (e.g., nitrogen, oxygen, silicon), and (3) chemical treatment of the carbon (e.g., boron, phosphorus, oxygen, halogens). One of the main problems is the actual location of the dopant atoms in the carbon network. They can be substituted to carbon in aromatic rings, located in interstitial sites, or most often, chemically bound to the edges of the carbonaceous macromolecules.

The lithium pre-doping hard carbon as anode material for lithium-ion battery can reduce irreversible capacity loss occurring at first charge/discharge process. The anode matching with $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes enhance the initial coulombic efficiency and produce higher energy density. The hard carbon without doping has reversible capacity of 149.8 mAh g^{-1} , while lithium pre-doped hard carbon has reversible capacity of 167.4 mAh g^{-1} at the current density of 20 mA g^{-1} (Hongbo *et al.*, 2015).

In most cases, the effect of doping on lithium electrochemical insertion is an increase in the reversible capacities, up to values of the order of $600\text{--}700 \text{ mAh g}^{-1}$. However, the potential profiles generally develop large hysteresis and large irreversible capacities. At the present time, unquestionable improvement in performance has been obtained in two cases: mild oxidation of graphite (Peled *et al.*, 1996) and boron doping (Way and Dahn, 1994).

Concluding Remarks and Trends

The use of carbons as a lithium reservoir in rechargeable batteries has led to what can now be considered as the major breakthrough in new practical battery systems in the second half of the twentieth century. A number of studies have been devoted to the search for alternatives to the carbon electrode (e.g., tin oxides, vanadate's, transition metal nitrides). Although these compounds may display large reversible capacities (up to 900 mAh g^{-1}), they also show large irreversible capacities and the potential versus lithium is markedly increased, which would result in a significant battery voltage drop.

Therefore, the use of carbons seems to be well established, at least in the medium term. Within this class of materials, development is still moving rapidly. The choice of a particular grade of carbon is always a compromise, based on consideration of electrode processing and costs. After the initial interest in noncrystalline carbons, the general trend among battery manufacturers has been to use crystalline carbons. Because of their good performance and low price, natural or synthetic graphite's, especially those enriched in rhombohedral phase, seem to be preferred by many manufacturers. Nevertheless, the versatility of the element carbon gives hope for future improvements. The use of nano-composite carbon material as electrodes for batteries will increase the surface area and thereby more current flows, which in turn increase the efficiency with less weight. Also, the use of nano materials decreases the time required to recharge a battery.

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Lithium and Sodium Layered Oxide Cathodes for Secondary Batteries: Structural and Electronic Considerations

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Abstract

With their high concentration of lithium/sodium to other elements, layered AMO_2 ($A = \text{Li}$ or Na , and $M =$ transition or post-transition metal) oxides have an unparalleled combination of specific capacity, high-voltage, and ability to insert/extract lithium or sodium at high rates. This combination of properties currently makes layered oxides the best option for lithium and sodium secondary batteries that have both high energy and power densities. This article highlights the general principles of the crystalline and electronic structure of layered lithium and sodium oxides as they pertain to the electrochemical performance of these materials in secondary batteries.

Key Points

- Highlight the diversity of structural nuances and electronic properties of layered oxides.
- Explore structure/property relationships in layered oxide cathodes for lithium and sodium secondary batteries.
- Correlate structural transitions to electrochemical behavior and intercalation chemistry in layered oxide materials.

Introduction

Layered AMO_2 oxides ($A = \text{Li}$ or Na , and $M =$ transition or post-transition metal) have remained technically important materials since the inception of the commercial lithium-ion battery with a layered LiCoO_2 cathode in 1991; they have also been intensely investigated as sodium-ion battery cathodes.

For secondary lithium batteries, layered LiMO_2 oxides reign supreme in terms of energy density and rate capability for practical application, although many other materials and structures have been investigated. However, even with their advantages over other known intercalation structures, layered LiMO_2 oxides are not without faults and require improvement to their performance. Thermal instability and cation mixing at high degrees of delithiation plague many layered compositions. LiCoO_2 is a well-known example; once more than 50% of the lithium has been removed from the structure, the material becomes thermally unstable and slight heating catalyzes oxygen loss due to the overlap between the electronic band attributed to the $\text{Co}^{3+/4+}$ redox couple and the filled O2p valence band (Amatucci *et al.*, 1996). This oxygen loss induces an irreversible structural transition to spinel Co_3O_4 . Nickel is a desirable replacement for cobalt as it is less expensive and can provide greater energy density. These benefits are not without consequence as the similarity in ionic radius between $\text{Ni}^{2+/3+}$ and Li^+ makes it difficult to synthesize and maintain during cycling a well-ordered layered LiNiO_2 or any layered composition where the ionic ratio of $\text{Ni}:\text{Li} \geq 0.8$ (Delmas *et al.*, 1997; Grundish *et al.*, 2019). Moreover, nickel does not provide any significant improvement in thermal stability of the layered structure over cobalt, although the degradation mechanism is different (Dahn *et al.*, 1994). Numerous studies have shown that mixing different ratios of transition-metals within the MO_2 layer of LiMO_2 compounds with a high degree of nickel can stabilize the structure and reduce cation mixing upon discharge, but other problems still plague these materials. Secondary particle cracking during cycling owing to large volume changes in the material through the various stages of lithiation/delithiation can cause delamination of the cathode active material from the other components in the cathode composite and result in severe performance degradation (Sun and Manthiram, 2017).

Sodium secondary batteries have gained renewed interest in recent years owing to the natural abundance of sodium and the ease with which ordered structures can be synthesized. For sodium secondary batteries, the competition between candidate cathode materials is more ambiguous with several structures showing promise. Layered Na_xMO_2 sodium cathodes maintain favor due to their high specific capacities relative to many other framework structures of interest, but they still suffer from structural deficiencies during cycling that result in impractical electrochemical profiles. Particularly, structural transitions and sodium ordering during intercalation/deintercalation yield voltage plateaus at irregular intervals that are often referred to as an electrochemical “Devil’s Staircase” (Vitoux *et al.*, 2017). To avoid these pitfalls, elemental doping of the M-site in Na_xMO_2 materials has been extensively explored (Kim *et al.*, 2011; Yang *et al.*, 2019). Moreover, specifically doping to induce vacancies in the M-site has been found to be a particularly interesting avenue of research (Ma *et al.*, 2017; de Boisse *et al.*, 2018). Despite the intense efforts to tailor the properties of layered sodium cathodes with these strategies, a suitable candidate for commercial sodium batteries has not yet been developed.

With layered oxide cathodes for lithium and sodium materials remaining of critical technical importance for current and future secondary batteries for portable and grid-scale energy storage, this article highlights the general principles of the crystalline and electronic structure of these materials as they pertain to their electrochemical performance in order to spur new developments in the field.

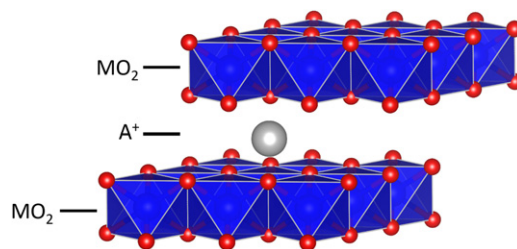


Fig. 1 General schematic of the AMO_2 layered oxide structure.

Structural Considerations

Structure of AMO_2 Layered Oxides

A general schematic for the structure of an AMO_2 oxide is shown in [Fig. 1](#). This structure consists of alternating MO_2 layers and alkali-ion layers; the MO_2 layers consist of edge-sharing MO_6 octahedra and the alkali-ion layers consist of edge-sharing AO_6 octahedra. Many alkali-ion layered oxides adopt the $\alpha\text{-NaFeO}_2$ structural prototype, which can be related to a classical cubic rock salt structure by ordering the alkali-ions and the transition-metal ions along one of the threefold unit cell axes. Thus, these materials have a close-packed oxygen sublattice with the oxygen packing having a strong influence on the type of sites present in the alkali-ion layer. The site occupancy of the alkali-ions can vary based on several factors that will be discussed further in this article. In short, there are three different sites alkali-ions can reside in: tetrahedral, octahedral, and trigonal prismatic. When synthesized directly via solid-state synthesis, many of these materials crystallize in the hexagonal or rhombohedral crystal system, unless there exists a factor that distorts the structure.

Unit cell distortions

There are two primary distortions that can occur in a layered oxide that can cause it to deviate from the hexagonal or rhombohedral crystal system – a monoclinic distortion and a triclinic distortion. A monoclinic distortion of the unit cell in a layered material is more common as it can be induced by several phenomena. Where the M site in an AMO_2 layered oxide is shared among several transition-metal or post transition-metal ions, a monoclinic distortion of the unit cell occurs if there is significant long-range ordering between the various ions occupying the M sites. This long-range order results in what is referred to as a “superstructure” within the material as there is additional ordering of the cations beyond that in a normal layered oxide. The formation of such a superstructure typically occurs where there is a size or charge mismatch among the ions in the M-site that makes ordering more thermodynamically favorable during synthesis. Alkali-ion ordering in the interlayer space during the intercalation/deintercalation process can also induce a monoclinic distortion of the unit cell of the material. The last circumstance in which this type of distortion can be observed is where there is a significant ratio of ions in the M-site with a localized electronic structure that can induce a cooperative Jahn-Teller distortion (see Section “Layered Lithium Oxides LiMO_2 ”). In more extreme cases, the unit cell can undergo a triclinic distortion. This type of distortion can occur where there is M-M intralayer bonding, a mismatch between the ordering in the MO_2 and the alkali-ion layer, or an extreme size mismatch between ions that occupy the M-sites ([Vitoux et al., 2020](#); [Yang et al., 2017](#)).

With various deviations to the layered structure able to occur that heavily influence the properties of these materials, a more convenient way to describe the nuanced structural information of a given compound is required to convey quickly and adequately the alkali-ion site occupancy between the MO_2 layers, the oxygen packing of the material, and any unit cell distortion.

Delmas notation

Alkali-ion layered materials are designated by a particular nomenclature set forth by [Delmas et al. \(1980\)](#). The notation starts with a letter that designates the site occupation of the alkali-ion in the alkali-ion layer between transition-metal layers – O for octahedral, T for tetrahedral, or P for prismatic – followed by a number that quantifies the number of transition-metal layers in the unit cell ([Fig. 2](#)). In the instance of a monoclinic distortion of the unit cell, a ‘ symbol is marked after the site occupation letter in the notation. Where a triclinic distortion occurs, a “ symbol is used following the site occupation letter. In the case of ion-exchanged materials where oxygen atoms do not remain on the same three positions of their original triangular lattice owing to one transition-metal layer shifting (0, 1/2, 0) during the exchange, a[#] is superscripted after the site occupation letter ([Carlier et al., 2002](#)). A general example for a layered material with a non-distorted unit cell is LiCoO_2 prepared via a traditional solid-state reaction, which has an O3-layered structure where the lithium atoms occupy octahedral sites between CoO_2 layers. Additionally, there are three CoO_2 layers within the unit cell for this material.

Oxygen packing

The primary convenience of the Delmas notation is its ability to convey quickly the oxygen packing, or alternatively, the MO_2 layer stacking in a material. The sequence of oxygen anions in the layered structure is important because it dictates the site coordination within the interlayer space that the alkali-ions can occupy as well as the structural transitions that are possible due to layer-gliding upon intercalation/deintercalation of lithium or sodium ions during electrochemical cycling or ion-exchange. [Fig. 2](#) provides a summary of

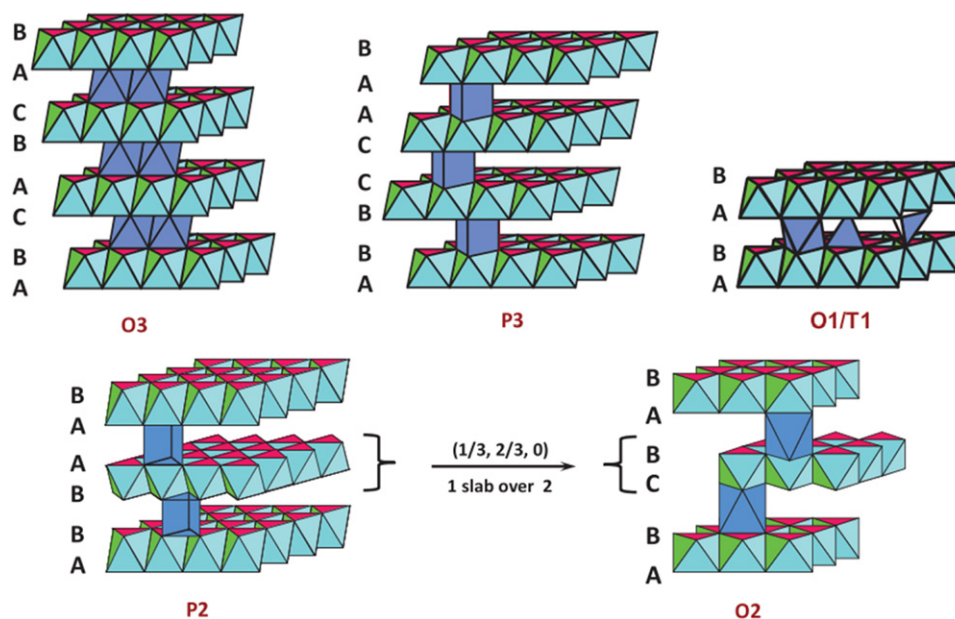


Fig. 2 Various oxygen packing permutations for the layered $A_x\text{MO}_2$ structure and their corresponding Delmas notation. Reproduced with permission Delmas, C., Carlier, D., Guignard, M., 2021. The layered oxides in lithium and sodium-ion batteries: A solid-state chemistry approach. *Adv. Energy Mater.* 11, 2001201. Available at: <https://doi.org/10.1002/aenm.202001201>. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

the many permutations of the layered $A_x\text{MO}_2$ structure along with their corresponding Delmas notation; these structures do not account for any potential distortions to the unit cell as all M-ions are considered to be the same (Delmas *et al.*, 2021).

An example of how the oxygen packing can dictate the crystallographic sites available in the interlayer space can be seen by comparing the P3 and the P2 layered structures. The P3 structure only has one type of orientation of the MO_6 octahedra in the transition-metal layers, resulting in every trigonal prismatic site in the adjacent alkali-ion layer face-sharing an MO_6 octahedron of one layer while edge-sharing three MO_6 octahedra of another layer. On the other hand, the P2 structure has two different MO_6 orientations that alternate between adjacent transition-metal layers, resulting in two types of trigonal prismatic sites in the interlayer space; one site is only face-sharing with adjacent MO_6 octahedra, and one site is only edge sharing with adjacent MO_6 octahedra. The oxygen packing of the O3 structure results in AO_6 octahedra that are only edge-sharing with MO_6 octahedra in the adjacent MO_2 layers.

The layer stacking of a layered material can usually be discerned by looking at the space group of which its X-ray diffraction pattern can be indexed, as well as the lattice parameters of its unit cell. Table 1 summarizes common space groups associated with various layer stacking motifs according to the Delmas notation. Once the space group of a material has been indexed, the number of stacking possibilities for its structure are drastically reduced, if not fully determined. From the space group there can be some ambiguity between the number of layers in the unit cell and, for sodium, whether the sodium are within octahedral or prismatic sites between the MO_2 layers – specifically when trying to determine between O3 and P3 layer stackings during the intercalation/deintercalation process.

Observation of the lattice parameter c gives a preliminary indication of the number of MO_2 layers in the unit cell for non-distorted layered materials if it cannot be discerned otherwise. The thickness of each $\text{A} + \text{MO}_2$ layer can be approximated as 5 Å for $\text{A} = \text{Li}^+$ or Na^+ ; thus, whatever multiple of 5 is closest to the value of c can be estimated as the number of MO_2 layers in the hexagonal unit cell. This method can be useful if there is ambiguity from the space group in determining whether a layered lithium material shows O2 or O4 stacking, or similarly, O3 or O6 layer stacking. However, the nature of the O6 layer stacking, which can be thought of as MO_2 layers having alternating O1 and O3 stacking with varying amounts of lithium in the interlayer space, is typically only observable at high degrees of delithiation.

If the composition of a material does not provide any insight for determining between O3 and P3 layer stacking for sodium compounds during the intercalation/deintercalation process, the ratio of diffraction intensities between the peaks attributed to the $(104)_{\text{hex}}$ and $(105)_{\text{hex}}$ planes of the hexagonal unit cell can be used to determine the sites present in the inter-layer space (Grundish *et al.*, 2020; Vitoux *et al.*, 2017). The $I_{(104)}/I_{(105)}$ ratio is smaller for compounds where sodium are in trigonal prismatic sites than for compounds where they sit in octahedral sites. Thus, if during the intercalation/deintercalation process $I_{(104)}/I_{(105)}$ decreases significantly, the layer stacking of the material can be presumed to have shifted from O3 to P3. These guidelines do not serve as a substitute for a full structural refinement of a material, but they can be used to gain quick insight on the layer stacking of a material if a full structural refinement cannot be performed, which is often the case for in-situ, in-operando, or ex-situ X-ray diffraction experiments for secondary battery electrode materials where they are not performed with a powerful radiation source. Solid-state nuclear magnetic resonance spectroscopy can also help

Table 1 Summary of common space groups for layered AMO_2 oxides with various stacking motifs

<i>MO₂ layer stacking</i>	<i>Space group</i>
Common MO₂ layer stackings	
O3	$R\bar{3}m$
P3	$R\bar{3}m$
P2	$P6_3/mcm$
Uncommon MO₂ layer stackings	
O1	$P\bar{3}m1$
O2	$P6_3mc$
O4	$P6_3mc$
O6	$R\bar{3}m$
OP4	$P6_3mc$
T [#] 2	$Cmca$
Distortions	
Monoclinic (example: O'3)	$C2/m$
Triclinic (example: O''3)	$P1$

elucidate specific alkali-ion environments within a structure in instances where a full refinement of the X-ray diffraction data is not possible (Clément *et al.*, 2015).

General Trends in Lithium and Sodium Layered Oxides

There are many differences between the layered oxides of lithium and sodium. The primary causes of many of these differences stems from the differences in ionic radii between sodium and lithium as well as the degree of ionicity between Na-O bonds versus Li-O bonds in these compounds; Na-O bonds are more ionic than their Li-O counterpart (Chen *et al.*, 2017; Delmas *et al.*, 2021). The trends discussed here are for as-synthesized compounds; differences and trends between layered lithium and sodium oxides related to their intercalation/deintercalation processes are reviewed in Section “Electrochemically Induced Structural Transitions in Layered Oxides”.

Layered sodium oxides Na_xMO_2 ($0.5 \leq x \leq 1$)

In general, sodium materials show a much richer structural diversity within the layered oxide framework depending on their composition than lithium layered oxides. A layered sodium compound can be directly synthesized with nearly all of the 3d transition metal elements, from titanium to nickel, and for some 4d transition metals owing to the large size and bonding differences between Na^+ and many transition metals. However, the ionicity of the Na-O bonds causes some transition metals to partially stabilize in the M^{4+} state rather than the M^{3+} state, resulting in sodium deficient stoichiometries that deviate from the fully occupied AMO_2 formula. These sodium deficiencies have a strong effect on the layer stacking of the resulting material. Compositions in the Na_xMO_2 system with $0.8 \leq x \leq 1$ show O3 layer stacking; for $0.6 \leq x \leq 0.8$, the materials show P2 layer stacking; and for compositions with $0.5 \leq x \leq 0.6$, the structure displays a P3 layer stacking (Fouassier *et al.*, 1973). These values are merely guidelines that can shift depending on the M-ion(s) present in the MO_2 layer of the material. Additionally, triclinic distortions of the unit cell have only been observed in sodium layered materials (Vitoux *et al.*, 2017; Yang *et al.*, 2017). Layered sodium positive electrode materials exhibit systematically lower voltages than layered lithium compounds beyond what is expected for switching the negative electrode from Li^+/Li to Na^+/Na because of the increased ionicity of the Na-O bond compared to that of the Li-O bond – this feature is covered more in-depth in the section on electronic considerations.

The size of sodium's ionic radius makes it unstable in tetrahedral sites within the layered structure, but it can still move from an octahedral site through a tetrahedral site to reach an adjacent octahedral site during intercalation/deintercalation as in the O3-layered compounds; the transfer from an octahedral to a tetrahedral site is a bottleneck in the diffusion process. This mechanism differs from that of the P2 and P3 compounds where sodium diffuses through face-sharing trigonal prismatic sites in the interlayer space. As a result, P2 and P3 layered materials generally show higher rate capabilities than their O3 counterparts.

Layered lithium oxides LiMO_2

Layered LiMO_2 compounds synthesized directly through solid-state synthesis mostly show the O3-layer stacking when synthesized by a direct solid-state method. Moreover, these compounds are always synthesized with full lithium content in the layer. For some 3d transition metals, the layered LiMO_2 structure cannot be obtained directly through solid-state synthesis owing to the similarity in the ionic radii of the M-ion and Li^+ . Other compounds can be synthesized in the layered structure, but with some antisite defects between Li^+ and the M^{3+} ion – LiNiO_2 is a well-characterized example. The small ionic radius of lithium allows it to occupy octahedral or tetrahedral sites within the structure with the ability to move through the structure from one octahedral site to another via an adjacent tetrahedral site without a significant bottleneck to the diffusion process. However, the tetrahedral sites in the lithium layer are face-sharing with MO_6 octahedra in the adjacent MO_2 layer, making them slightly higher in energy relative to the octahedral sites. Moreover, the distance between oxygen ions in adjacent MO_2 layers effects the barrier to lithium diffusion in

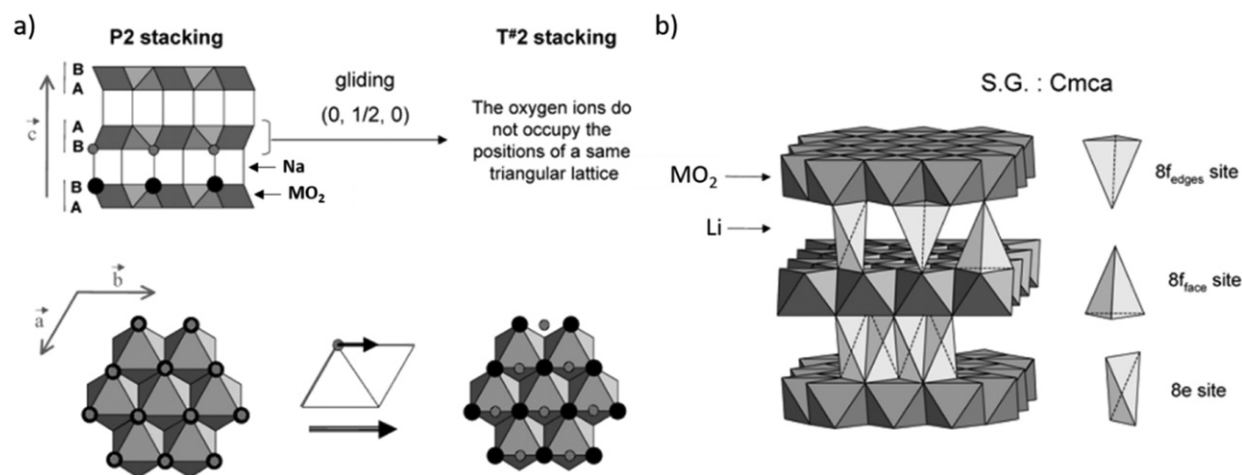


Fig. 3 (a) Layer gliding involved in the $P2 \rightarrow T^{\#}2$ transformation occurring during ion-exchange from sodium to lithium. The ion-exchange process is shown along the (110) plane and from a top view of the interslab space. The oxygen layers at the bottom (dark circles) and at the top (hatched circles) of one interlayer space are highlighted. (b) Resulting structure of a $T^{\#}2$ layered LiMO_2 after ion-exchange; the distorted tetrahedral sites available for the Li^+ -ion occupation are also presented. Reproduced with permission Tournadre, F., Croguennec, L., Saadoun, I., *et al.*, 2004. The $T^{\#}2\text{-Li}_{2/3}\text{Co}_{2/3}\text{Mn}_{1/3}\text{O}_2$ system. 1. Its structural characterization. *Chem. Mater.* 16, 1411–1417. Available at: <https://doi.org/10.1021/cm035176p>. Copyright 2004 American Chemical Society.

the interlayer space (Kang and Ceder, 2006). Lithium is not stable in trigonal prismatic sites between the MO_2 layers. Thus, as-synthesized P2 and P3-layered Li_xMO_2 compounds have yet to be observed. Even layered P2 or P3-layered Na_xMO_2 sodium compounds that have been ion-exchanged for lithium do not show trigonal prismatic sites in the lithium layer.

Ion exchanging layered sodium compounds for lithium can result in metastable materials with unusual layer stackings that cannot be directly synthesized with lithium precursors. Two examples of this are shown by $\text{O}2\text{-LiCoO}_2$ and $T^{\#}2\text{-Li}_{2/3}\text{Co}_{2/3}\text{Mn}_{1/3}\text{O}_2$, both synthesized via ion-exchange from their sodium counterparts. In the case of the $\text{O}2\text{-LiCoO}_2$, as-synthesized $\text{Na}_{0.7}\text{CoO}_2$ adopts a P2 layer stacking (Carlier *et al.*, 2002). As lithium is exchanged for sodium in this material, any Co^{4+} is reduced to Co^{3+} to accommodate a fully lithiated structure. Additionally, the MO_2 layers glide to form octahedral sites instead of trigonal prismatic sites to accommodate the smaller size of lithium, but do not change orientation. Maintaining the MO_2 orientation results in two CoO_2 layers remaining in the unit cell after the exchange process, resulting in the final $\text{O}2\text{-LiCoO}_2$ product. For $T^{\#}2\text{-Li}_{2/3}\text{Co}_{2/3}\text{Mn}_{1/3}\text{O}_2$, Mn^{4+} and Co^{3+} do not reduce during the exchange process. However, with lithium unstable in trigonal prismatic sites, the oxygen atoms of one of the MO_2 layers glide $(0, \frac{1}{2}, 0)$, as shown in Fig. 3(a), to form tetrahedral sites in which lithium ions can reside (Tournadre *et al.*, 2004). The resulting $T^{\#}2$ layered structure with distorted tetrahedra occupied by lithium is shown in Fig. 3(b). The ion exchange method has been shown to be the only way to synthesize a lithium layered oxide where lithium exclusively occupies tetrahedral sites or with an even number of MO_2 layers in the unit cell of the material.

Electrochemically Induced Structural Transitions in Layered Oxides

Layered oxides can be prone to exhibit structural transformations during the intercalation/deintercalation process. Many layered sodium compounds demonstrate gliding of the MO_2 layers during insertion/extraction of sodium, which causes a transition from one type of layered stacking to another. This phenomenon can result in numerous potential plateaus for a material in the composition range where these transitions occur, making them impractical as positive electrodes for commercial batteries. Lithium compounds do not typically exhibit MO_2 layer gliding as readily as sodium compounds. Instead, lithium compounds are more susceptible to transition-metal migration from the MO_2 layer to the lithium layer that induces layered to rock-salt or layered to spinel phase transformations, especially with 3d-transition-metals such as Mn and Ni.

MO_2 layer gliding

Layered materials can exhibit gliding of the MO_2 layers during intercalation/deintercalation of sodium or lithium. This phenomenon is much more common in intermediate compositions of Na_xMO_2 compounds than for Li_xMO_2 compounds. Shifting of the MO_2 layers in Li_xMO_2 does not occur until a high degree of delithiation (low value of x), if at all, to maintain the stability of the layered structure via the formation of metastable layer stacking (Chen *et al.*, 2002). Transitions from one layer-stacking sequence to another during intercalation/deintercalation can only occur between stacking sequences that have the same MO_2 layer orientations. For example, transitions between O3, P3, and O1 or between P2 and O2 are allowable – see Fig. 2. However, transitions between these two sets would require a 180° rotation about the c -axis for one of the MO_2 layers, which cannot occur during cycling.

The transition from one layered phase to another is associated with a two-phase thermodynamic equilibrium where the phases themselves do not change, only their ratio changes within the cathode particles, which fixes its voltage during the electrochemical

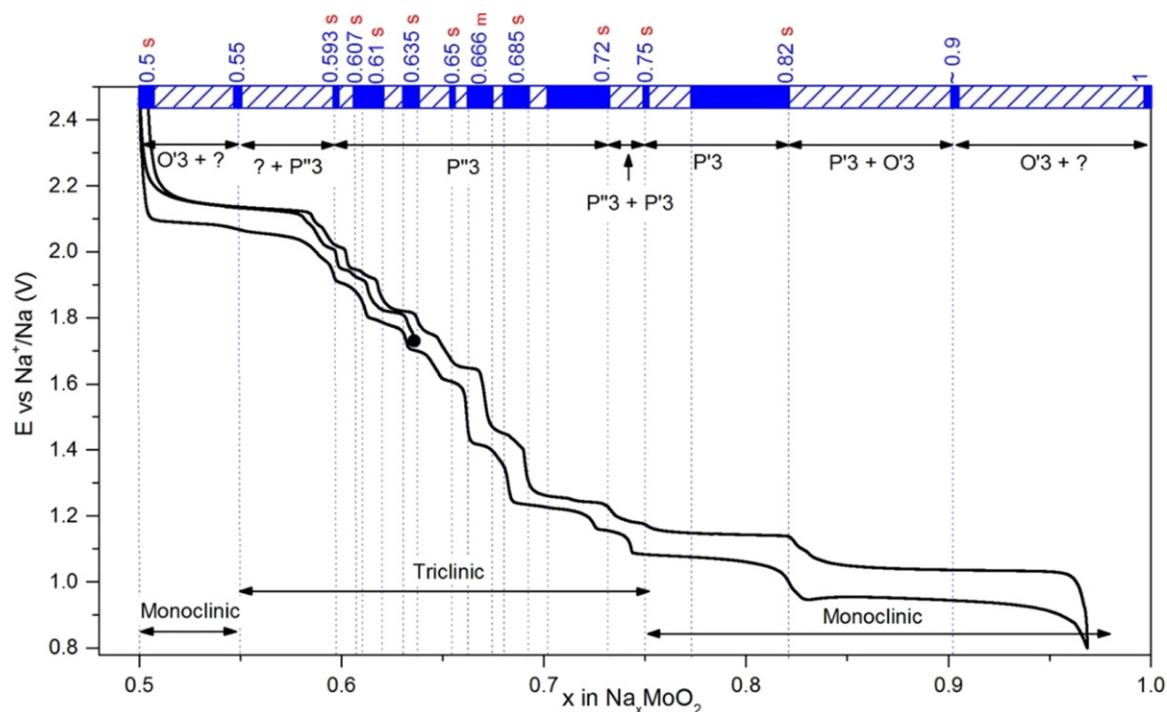


Fig. 4 Voltage-composition curve for the layered Na_xMoO_2 system. Reproduced with permission Vitoux, L., Guignard, M., Suchomel, M.R., *et al.*, 2017. The Na_xMoO_2 phase diagram ($1/2 \leq x < 1$): An electrochemical devil's staircase. *Chem. Mater.* 29, 7243–7254. Available at: <https://doi.org/10.1021/acs.chemmater.7b01834>. Copyright 2017 American Chemical Society.

intercalation/deintercalation process and can cause numerous voltage plateaus over a wide composition range for a material. **Fig. 4** shows a severe example of the effect of these two-phase regions on the electrochemical character of Na_xMoO_2 (Vitoux *et al.*, 2017). Such transitions in a positive electrode material make it difficult to design practical batteries for commercial applications owing to the electrochemical performance and the repeated structural changes upon repeated long-term insertion/extraction of alkali-ions. It should be noted that a similar effect occurs in the voltage-composition curve of a layered A_xMO_2 material due to vacancy ordering, which is covered more in depth in Section “Vacancy ordering”.

Layered to rock salt and layered to spinel transformations

Transition-metal migration from the MO_2 layer to an octahedral site in an adjacent lithium layer during electrochemical intercalation/deintercalation of lithium from Li_xMO_2 compounds can transform its structure from layered to rock salt or spinel (Bak *et al.*, 2014; Luo *et al.*, 2016; Mu *et al.*, 2018). This phenomenon is less common in Na_xMO_2 materials owing to the larger size of the sodium octahedral-sites relative to the ionic radius of the M-ions in these materials. Additionally, the formation of trigonal prismatic sites in the sodium layer space prevents transition-metals from migrating to the interlayer space. Although some transition-metals migrate more readily than others depending on their crystal field stabilization energy (see Section “Crystal Field Stabilization Energy”), even transition-metals with a strong octahedral site preference energy have been shown to be able to migrate from an octahedral site in the MO_2 layer, through a tetrahedral site in the lithium layer, to finally occupy an octahedral site in the lithium layer; **Fig. 5** summarizes this migration pathway for the layered to spinel transformation (Croguennec and Palacin, 2015). A layered to rock salt transformation is a case of more transition-metals migrating to occupy the interlayer space than in the layered to spinel case as well as a loss of structural oxygen. Formation of a rock salt structure is severely detrimental to electrochemical performance as the migrating transition-metals block the diffusion pathway for lithium to reinsert into the structure (Kuriyama *et al.*, 2015).

Electronic Considerations

The electronic properties of each constituent ion in positive electrode materials control the A-O and M-O bond characteristics that effect their crystalline and electronic structure. Observation of certain structural features can often provide qualitative insight into the electronic structure of the material that will dictate its electrochemical response to intercalation/deintercalation. However, a greater knowledge of the electronic behavior in positive electrode materials is necessary to explain some of their structural phenomena and the origin of the redox potentials observed in these compounds. The following section details important electronic considerations for lithium and sodium layered A_xMO_2 oxide positive electrode materials.

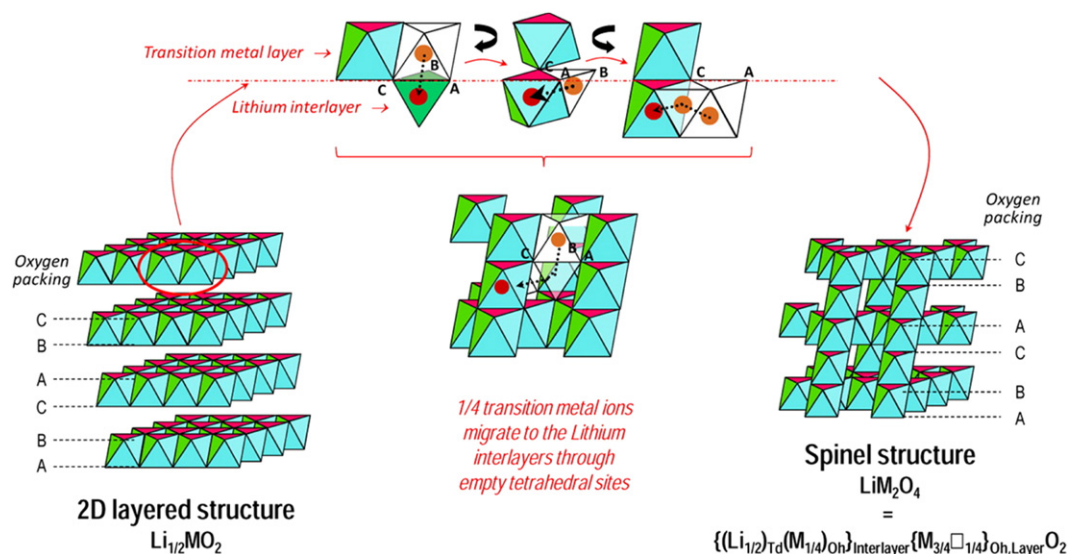


Fig. 5 Migration mechanism for transition-metals in the LiMO_2 structure to induce layer-spinel or layered-rock salt phase transformations. Reproduced with permission Croguennec, L., Palacin, M.R., 2015. Recent achievements on inorganic electrode materials for lithium-ion batteries. J. Am. Chem. Soc. 137, 3140–3156. Available at: <https://doi.org/10.1021/ja507828x>. Copyright 2015 American Chemical Society.

Coulombic Interactions

Static charge arguments can rationalize the lack of formation of certain layer stackings and vacancy ordering in the alkali-ion layer during cycling in layered A_xMO_2 materials. The coordination between $(\text{A},\text{M})\text{O}_x$ polyhedra is a structural descriptor for the level of $(\text{A},\text{M})\text{-O-(A},\text{M})$ interaction as the greater the coordination of the two polyhedra, the shorter the distance between the two cations. Thus, two cations sitting in corner sharing polyhedra will have less interaction than two cations sitting in edge-sharing polyhedra. Face-sharing polyhedra have the greatest degree of electrostatic interaction between the two cations sitting in these polyhedra (Pauling, 1960). The Coulombic interaction between cations can lead to phenomena that have an adverse effect on the structure and electrochemical profile of layered oxide cathodes.

Vacancy ordering

Alkali-ion ordering in the interlayer space can occur upon deintercalation from A_xMO_2 materials, resulting in certain crystallographic sites becoming preferentially vacant (Reimers and Dahn, 1992; Toumar *et al.*, 2015). Vacancy ordering is the result of interlayer and intralayer coulombic interactions between A-M ions and A-A ions, respectively. Although vacancy ordering in the interlayer space can occur in Li_xMO_2 compounds, it is much more common in Na_xMO_2 materials since Na-Na repulsions are stronger than Li-Li repulsions owing to sodium's larger size and more ionic character. Moreover, prismatic sites in the interlayer space for many sodium compounds are face-sharing, which allows for faster Na-ion diffusion in the layer, but also allows for greater Na-Na interactions. This greater degree of interaction results in stronger ordering compared to edge-sharing octahedra for octahedral sites in the interlayer space.

Interlayer A-M interactions can also induce A-ion ordering between the MO_2 layers. For lithium compounds, this phenomenon can occur in delithiated Li_xMO_2 phases where there is ordering of the M-ions in the MO_2 layer. If additional M' -ion species are introduced into the MO_2 layer to induce disorder in this layer, Li-ordering will not occur in the adjacent interlayer space. For sodium, inducing disorder in the MO_2 layers can aid in preventing Na-ordering in the interlayer space, but the Na-Na interactions within the layer, especially for P2 and P3 compounds, can still induce sodium ordering. A-ion ordering results in a step in the potential curve of the material for the same transition-metal redox couple, like that of a layered-layered phase transition. This effect can be observed in Fig. 4 for layered Na_xMoO_2 in the composition range of $0.593 < x < 0.72$ where there is no transition from the P'3 phase, but numerous voltage plateaus occur due to sodium ordering in the interlayer space.

Metastable phases

Owing to the site coordination between the A-ions in the interlayer space and the MO_2 layers resulting in strong coulombic repulsions, certain layer stackings are metastable and cannot be synthesized directly with solid-state synthesis. Additionally, strong repulsions between oxygen-ions in adjacent MO_2 layers at high levels of deintercalation can result in MO_2 layer shifts for O3- Li_xMO_2 and P2- Na_xMO_2 materials. In the O2 and O4 layer stackings, each AO_6 octahedron shares a face with an adjacent MO_6 octahedron. Thus, the coulombic interactions between A-ions and M-ions cause these layered structures to be less stable. O2 and O4 lithium layered compounds are only obtainable via ion-exchange with partially sodiated P2 or OP4 layered counterparts, respectively. O2 sodium compounds are typically only obtained at high levels of deintercalation from a P2- Na_xMO_2 material. O1 layer stackings for lithium can occur at extreme levels of delithiation from an O3- LiMO_2 starting material where the interlayer

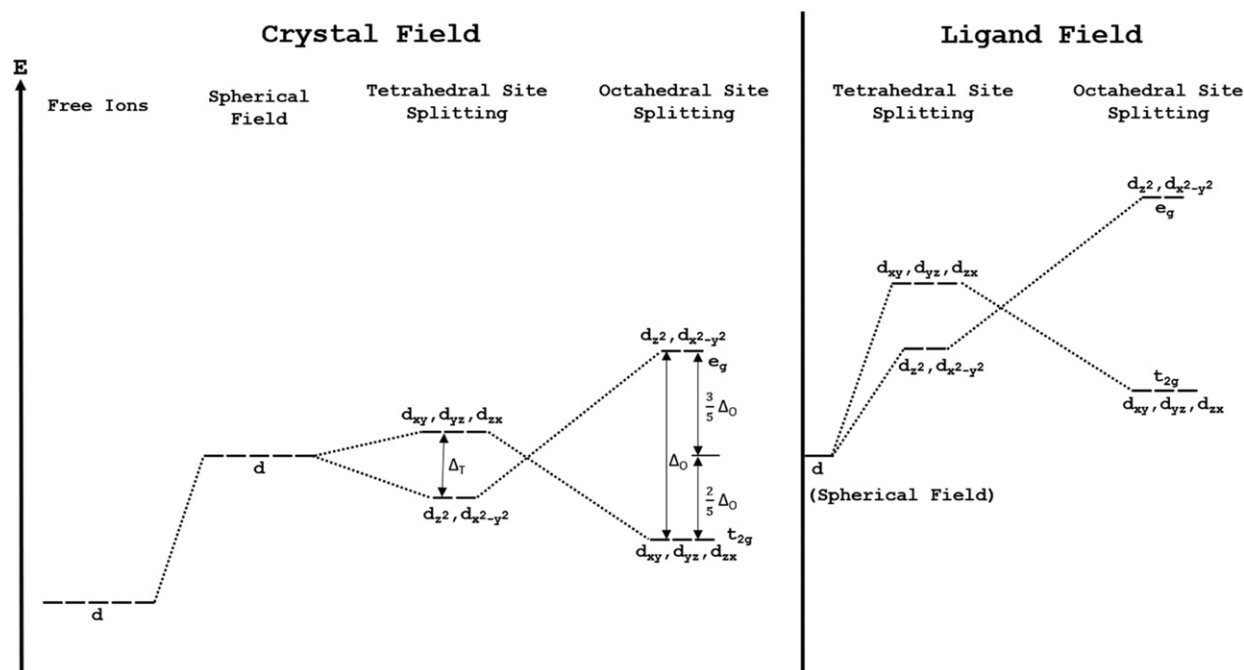


Fig. 6 Evolution of the d-orbital energy levels in a purely ionic (crystal field) model, and after considering orbital interactions with nearest neighbor anions (ligand field). Reproduced from Cox, P.A., 2010. *Transition Metal Oxides An Introduction to Their Electronic Structure and Properties*, Oxford University Press. West, A.R., 2014. *Solid State Chemistry and its Applications*, second ed. John Wiley and Sons, Ltd.

distance becomes small enough for the orbitals of the oxygen-ions in adjacent MO_2 to interact and repel each other, shifting the layers in such a way that there is only one MO_2 layer per unit cell (Amatucci *et al.*, 1996).

Electrons in Transition-Metals and Redox Potentials

Electronic properties of the M-ion layered A_xMO_2 oxides have a strong effect on the structure and electrochemical properties of the material. This section aims to provide insight into the effects of the d-electrons of transition-metals on the structure of A_xMO_2 oxides and the origin of the redox potential for classical positive electrodes that compensate lithium or sodium deintercalation with a transition-metal redox couple.

Crystal-field and ligand-field considerations

For a free transition-metal ion in vacuum, the five d-orbitals are degenerate in energy. In a crystal, the degeneracy is lifted in accordance with the site geometry of the transition-metal due to the surrounding anions affecting the energy required to place an electron in each orbital. This phenomenon results in the d orbitals that sit nearer to the surrounding anion orbitals being higher in energy than the orbitals that are farther away. If the orbitals of the surrounding anions are assumed to be point charges, the total energy of the d orbitals is conserved relative to their initial energy. However, if the wave functions of the anion orbitals surrounding the transition-metal are considered, the energy of the d orbital manifold is no longer conserved. The difference between these two assumptions, point-charge versus anion orbitals, is the fundamental difference between Crystal Field Theory and Ligand Field Theory. In other terms, crystal field theory can be considered a purely ionic model, whereas ligand field theory is a cluster model which has components of molecular orbital theory (Ballhausen, 1962). Fig. 6 shows an approximation of the energy evolution of the d-orbitals in a generic transition-metal from a free-ion, to sitting in a spherical charge field, and finally to the more applicable scenarios of sitting in a tetrahedral or octahedral site under point charge and ligand field assumptions (Cox, 2010; West, 2014).

Filling of the electronic states of the d-orbitals of the same energy occurs according to Hund's rule of maximum multiplicity; however, different possible spin configurations are possible when electrons populate the lower and higher lying d-electron states. If the splitting energy – the energy between the lower lying d-electron states and the higher energy states, denoted as Δ – is greater than the pairing energy – the energy required to pair an electron of opposite spin into an orbital with a preexisting electron, denoted as P – then a low spin (LS) electron configuration will occur where all of the lower energy orbitals are completely filled with two electrons of opposite spin, before an electron occupies a higher energy orbital. If $P > \Delta$, then the electrons are in a high spin (HS) configuration where all the d-orbitals are singly filled with an electron of like spin before an electron of opposite spin occupies any of the orbitals. The competition between these two spin states is most prevalent in 3d transition-metals where Δ is low enough for them to occur; 4d and 5d transition-metals rarely display HS configurations. The spin configuration can play an important role in the stabilization of transition-metal ions in octahedral versus tetrahedral sites. The spin state of a transition-metal generally does not

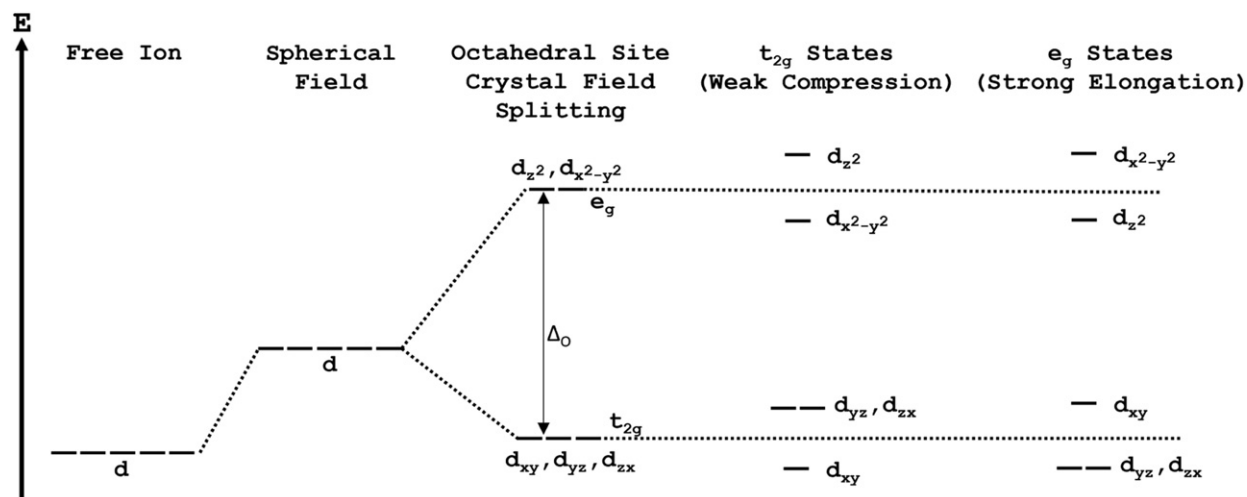


Fig. 7 d orbital energy levels for a weak and strong Jahn-Teller Distortions relative to t_{2g} and e_g orbitals of a normal octahedral site in the ionic model.

change once a material is synthesized, but spin crossover can be induced via external stimuli, such as high-pressure or light. A specific instance has been observed for a redox driven spin transition from HS Co^{2+} to LS Co^{3+} upon deintercalation of sodium from O3-layered $\text{NaTi}_{0.5}\text{Co}_{0.5}\text{O}_2$. Upon intercalation of sodium back into the material, Co^{2+} reverts to a HS configuration, but the voltage hysteresis between the charge and discharge process is about 3 V, which is much larger than for a traditional transition metal redox couple with a constant spin configuration (Watanabe *et al.*, 2019).

Crystal field stabilization energy

In the ionic model, the higher energy e_g orbitals of an octahedral site are destabilized from the level of the degenerate d orbitals in a spherical charge field by $0.6 \Delta_O$; the lower energy t_{2g} orbitals are stabilized by $-0.4 \Delta_O$. The tetrahedral site splitting energy (Δ_T) and the octahedral site splitting energy (Δ_O) can be related through the approximation $\Delta_T \approx \frac{4}{9} \Delta_O$. If the spin state of a transition-metal is known, its energy in an octahedral site can be compared to its energy in a tetrahedral site to provide insight into site occupation preference and whether the M-ion will migrate out of its MO_6 octahedra into the alkali-ion layer to induce a structural transition from the layered LiMO_2 phase (Reed and Ceder, 2004). The level of excess energy that an M-ion has in an octahedral site indicates its ability to move within the structure during the intercalation/deintercalation process. For example, Ni^{2+} (d^8) has a stabilization of $-1.2\Delta_O$ in an octahedral site compared to $-0.533 \Delta_O$ in a tetrahedral site, giving it a strong octahedral site preference. On the other hand, Ti^{3+} (d^1) has an octahedral stabilization of $-0.4 \Delta_O$ and a tetrahedral stabilization of $-0.178 \Delta_O$, indicating it is less stable than Ni^{2+} in an octahedral site and more likely to migrate within the structure of a material. HS d^5 M-ions, such as Mn^{2+} and Fe^{3+} , have no stabilization in an octahedral site compared to a tetrahedral site and can easily migrate within the structure.

Jahn-Teller distortions in solids

Uneven filling of degenerate d-orbital states for an M-ion in an octahedral site can lead to distortions of the MO_6 octahedra. A single electron residing in the t_{2g} orbitals for d^1 transition-metals can induce a weak Jahn-Teller (JT) distortion where two of the M-O bonds along a single axial component in the MO_6 octahedra compress. Uneven filling of the e_g orbitals, as in HS d^4 ($t_{2g}^3 e_g^1$), LS d^7 ($t_{2g}^6 e_g^1$), and d^9 result in a stronger JT distortion in which the M-O bonds along a single axis elongate to form a more square planar coordination. In each case – M-O bond compression and M-O bond elongation – the degeneracy of the t_{2g} and e_g orbitals is removed. Fig. 7 depicts the orbital energy level splitting of an M-ion in an octahedral site with uneven filling of the t_{2g} and e_g orbitals. It is possible for uneven filling of the e_g orbitals to result in both a positive JT distortion (2 elongated and 4 shortened bonds) and a negative JT distortion (2 shortened and 4 elongated bonds); the positive JT distortion is typically witnessed in real materials owing to anharmonic effects (Khomskii and van den Brink, 2000). The electronic states of a negative e_g distortion would effectively look the same as the t_{2g} states distortion shown in Fig. 7 (Radin and Van der Ven, 2018).

If enough M-ions have a distortion in their octahedra, a cooperative JT distortion occurs that can result, for example, in a monoclinic distortion of a hexagonal unit cell. For layered lithium compounds, the observation of a cooperative JT distortion usually occurs during the deintercalation process since the layered LiMO_2 structure cannot be stabilized with JT active M-ions that do not have a strong octahedral site preference, such as Ti^{3+} (d^1 : t_{2g}^1 : weak JT distortion) and Mn^{3+} (d^4 : $t_{2g}^3 e_g^1$: strong JT distortion). Layered Na_xMO_2 materials can be directly synthesized with these ions and exhibit a monoclinic distortion to their unit cell upon direct synthesis of materials with a strong JT active ion, such as NaMnO_2 (Parant *et al.*, 1971). Layered Na_xMO_2 where the M-ion has a weak JT distortion retains a hexagonal unit cell.

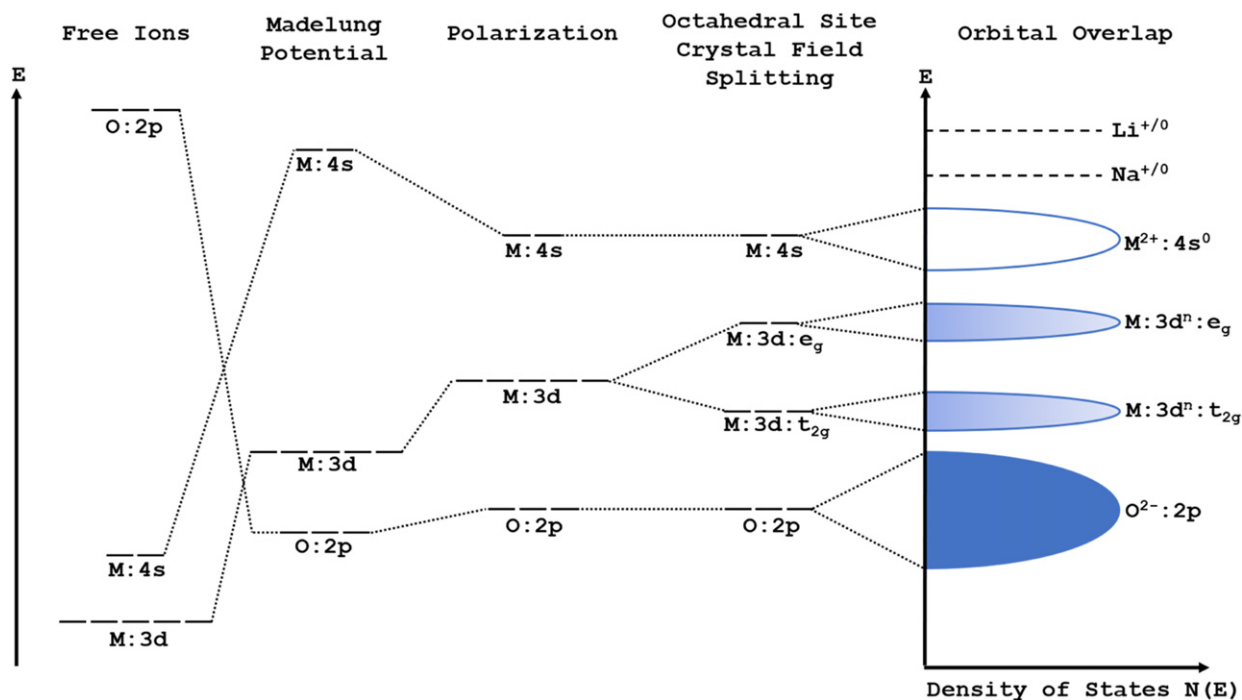


Fig. 8 Construction of localized-electron configuration for a 3d transition-metal oxide compound with the ionic model; orbital overlap can be used to widen these discrete energy levels into bands. Adapted from Cox, P.A., 2010. Transition Metal Oxides An Introduction to Their Electronic Structure and Properties. Oxford University Press.

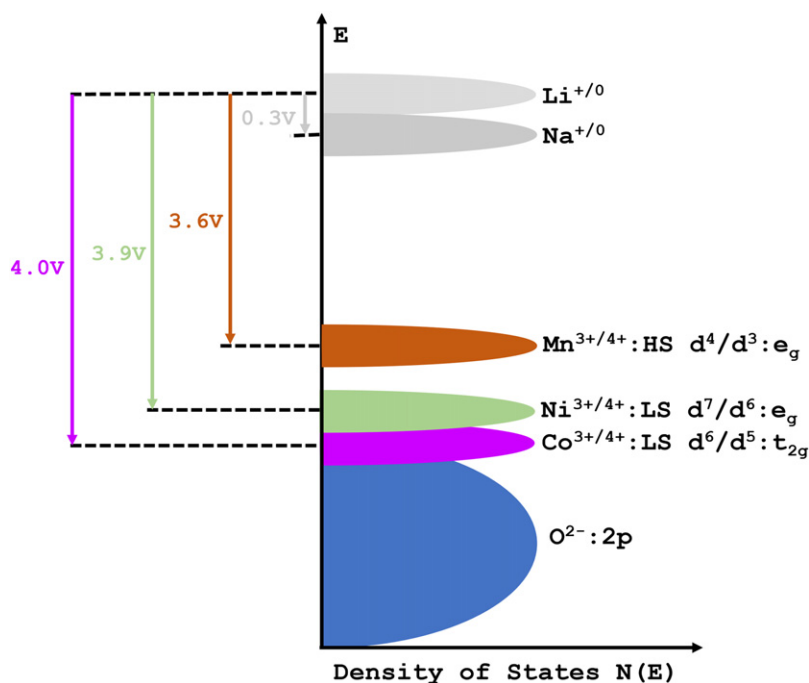


Fig. 9 Relative M:3d band energies (redox couples) for common M-ions in Li_xMO_2 oxides, relative to $Li^{+/0}$.

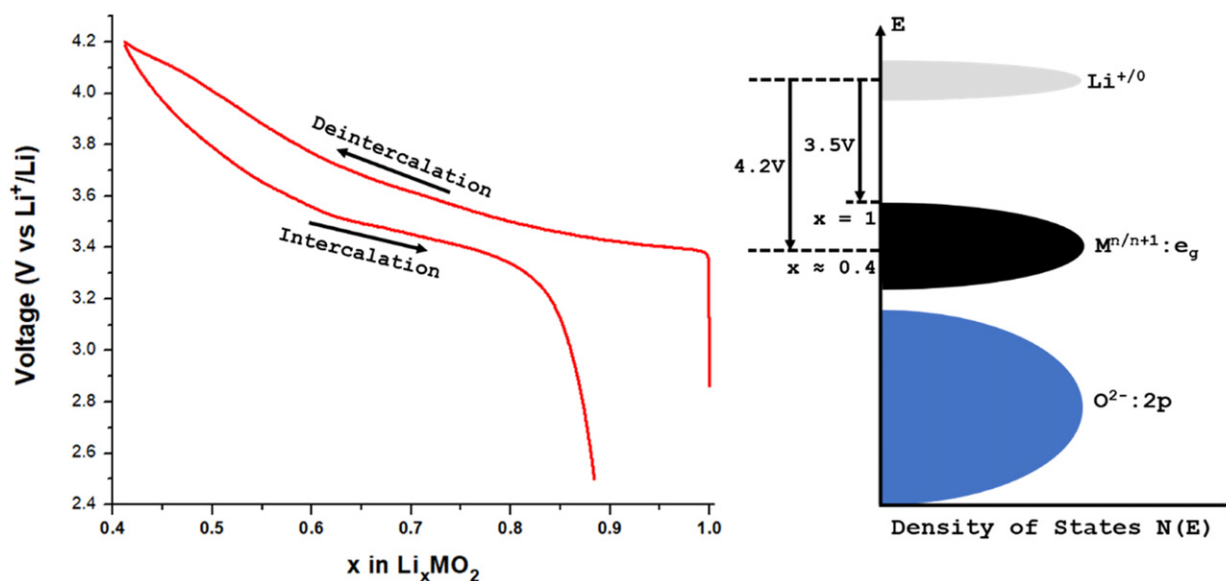


Fig. 10 Correlation of the electrochemical intercalation/deintercalation process and the addition/removal of electrons from the transition-metal band for a generic LiMO_2 positive electrode operating on a transition-metal redox couple $\text{M}^{n/n+1}$ occurring in the e_g band.

Transition-metal redox potentials

Fig. 8 qualitatively extends the ionic model to a full crystalline solid for a transition-metal oxide. The free-ion energies are first corrected by a Madelung potential, which is the electrostatic energy gained by arranging the ions in a crystalline lattice, on estimating each ion as a point charge (Kittel, 2005). The second correction comes from the site polarization that occurs whenever charges are moved through a lattice; this effect lowers the energy of empty orbitals and raises the energy of filled orbitals. After accounting for crystal field effects for the transition-metal d orbitals, the individual atomic energy levels can be broadened into bands by considering orbital overlap between ions. The point charge assumption of the ionic model makes orbital overlap impossible to estimate; it must be experimentally measured or simulated. However, this illustration provides intuition on the nature of transition-metal redox couples relative to the O2p valence band and M4s conduction band.

In this model, each band can be directly attributed to a set of atomic orbital states. Thus, the filled valence band has only O2p character and the conduction band is composed of empty M4s states. The d orbital states lie within the band gap; their level of occupancy is dictated by the number of d electrons localized on the transition-metal and the concepts outlined earlier in this section. If a positive electrode material compensates the charge loss/gain of a Li^+ or Na^+ -ion from its structure during deintercalation/intercalation with the reversible oxidation/reduction of a transition-metal ion, then the position of the highest filled t_{2g} or e_g band determines the operating voltage of that material during charge/discharge. Each single electron redox couple of $\text{M}^{n/n+1}$ has an associated voltage. **Fig. 9** depicts redox couples relative to the $\text{Li}^{+}/0$ couple of lithium metal for desirable M-ions in the layered Li_xMO_2 structure. Note the overlap between the LS $\text{Co}^{3+/4+}$ t_{2g} band with the top of the O2p band, which results in oxygen loss and a layered to spinel phase transformation when the material is delithiated and heated.

Owing to the pairing energy for two electrons of opposite spin to occupy the same orbital, each set of localized d orbitals in an octahedral field can be thought of as having two electron bands that are unequal in energy, one for spin up ($\uparrow$), and one for spin down ($\downarrow$). When referring to a full band, only the highest occupied band corresponding to a single electron spin must be filled for the material to be electronically insulating.

Fig. 10 illustrates an $\text{M}^{n/n+1}$ redox couple in the e_g band of a generic layered Li_xMO_2 material assuming a fully occupied d orbital band in the fully intercalated material and no structural transitions or vacancy ordering occur during the insertion/extraction process. This diagram illustrates how the electronic structure of transition-metal oxides changes during battery cycling and can be tailored through intercalation chemistry, allowing for fundamental physical properties of the material to be studied in addition to evaluating its performance as a battery electrode material. For oxygen redox materials, the O2p band is sufficiently high in energy and there is enough excess alkali-ions in the material that electrons can be removed from the O2p band to compensate for alkali-ion insertion/extraction in place of or in addition to transition-metal redox (House *et al.*, 2020).

The inductive effect

The ionic model is sufficient for qualitatively understanding the origin of the transition-metal redox potential in intercalation-based positive electrodes; however, it does not accurately describe why certain materials exhibit drastically different potentials for the same redox couple. To describe this phenomenon, a cluster model is necessary that accounts for atomic orbital mixing and M-O bond character. Additionally, next nearest neighbor interactions across a common oxygen ion – M-O-M or X-O-M interactions (where X is a transition-metal, post transition-metal, or a non-metal in a polyanionic complex) – play an important role in

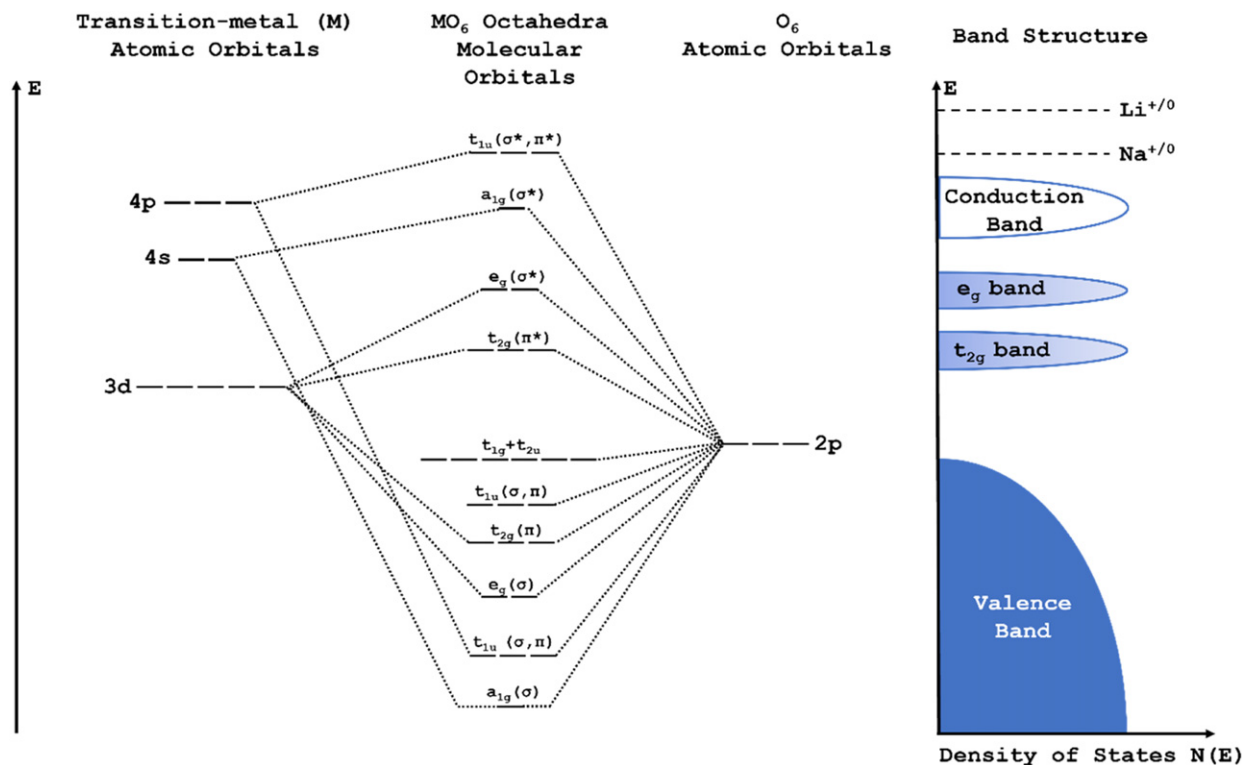


Fig. 11 Orbital mixing between a transition-metal (M) ion and oxygen anions for an MO_6 octahedra according to molecular orbital theory.

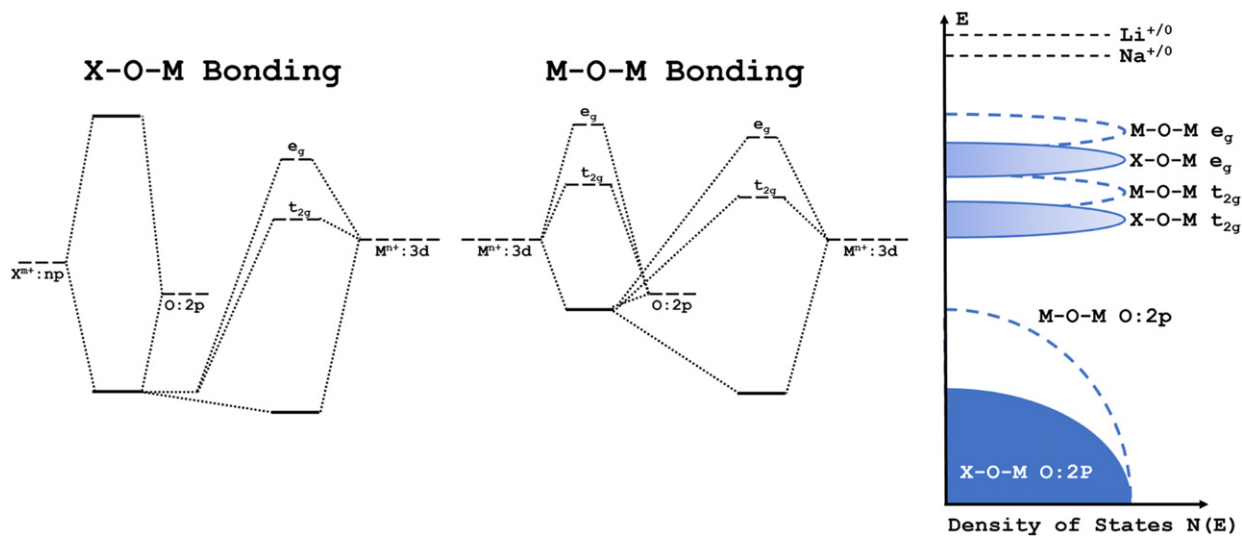


Fig. 12 Schematic of X-O-M and M-O-M orbital interactions and their effect on the M-O orbital mixing, resulting in the shifting of the bands of primarily transition-metal character; the inductive effect.

shifting the position of the transition-metal d orbitals in the final electronic structure of a material. Fig. 11 depicts the orbital mixing between a transition-metal ion and surrounding oxygen anions in an MO_6 octahedron in MO theory. The bonding molecular orbitals are localized more on the oxygen ions while the antibonding molecular orbitals have more transition-metal character (Cox, 2010). An approximated band structure for a simple MO_6 octahedron yields a similar result as in the ionic model, with the filled valence band primarily having $\text{O}2p$ character and the transition-metal states of varying occupancy residing within the band gap of the material.

Extending this model to next nearest neighbor atoms across a common oxygen ion yields the orbital mixing shown in Fig. 12 for an M-O-M interaction and an X-O-M interaction. This schematic assumes $\text{X}^{\text{m}+}$ bonds more covalently with oxygen than the

M^{n+} ion, which weakens the M-O bond in the X-O-M linkage. The degree of covalent mixing between M orbitals and oxygen orbitals determines the bond strength, and consequently the energy of the orbitals. Stronger M-O bonds – more covalent mixing between M3d and O2p orbitals – introduces a repulsion between the bonding and antibonding orbitals, which raises the energy of the t_{2g} (π^*) and e_g (σ^*) orbitals, lowering the operating voltage (i.e. the potential difference between the transition-metal redox potential and $Li^{+/0}$) of the transition-metal redox couple compared to an M-O-M linkage. Conversely, weaker M-O bonding induced from strong X-O covalent bonding lowers the energy of the t_{2g} (π^*) and e_g (σ^*) orbitals, raising the operating voltage of the transition-metal redox couple. This phenomenon is known as the inductive effect and is most prevalent in transition-metal redox couples observed between different polyanion framework structures (Manthiram and Goodenough, 1989, 1987; Padhi *et al.*, 1997). However, a similar effect has been observed in layered A_xMO_2 oxides where the M-ion site is partially occupied with high-valent Sb^{5+} and Te^{6+} in normal octahedral sites (Sathiya *et al.*, 2013; Yuan *et al.*, 2014). This finding suggests that the tailoring of a transition-metal redox potential via the inductive effect can now be extended to layered A_xMO_2 materials, opening a new pathway for materials design in these compounds.

Electronic conduction

A material does not need to have good electronic conductivity to serve as an electrode, but it can aid in the voltage overpotential of the intercalation/deintercalation process, especially at high current densities. Continuing with the simplified band picture for transition-metal compounds developed in Fig. 8, if the highest occupied d orbital of the transition-metal is completely filled, then the material is an electronic insulator. If the highest occupied d orbital of the transition-metal is only partially filled, then the material is normally an electronic conductor, either polaronic or metallic. However, intercalation compounds can undergo unique electronic transitions as their electronic structure changes during the insertion/extraction of alkali-ions. Layered lithium cobalt oxide is a prime example of this phenomenon as it undergoes a first-order Mott transition (electronic insulator to metallic conduction) once enough Li^+ -ions have been removed from the initially full t_{2g} band in $LiCoO_2$ ($LS\ Co^{3+}: t_{2g}^6 e_g^0$), forming holes in the band to allow for electrons to conduct in Li_xCoO_2 ($x < 0.75$) (Marianetti *et al.*, 2004).

$LiFePO_4$ is an achitypal example of a small polaron conductor in which electronic conduction takes place via the hopping of localized holes between Fe^{2+} and Fe^{3+} sites (Zaghib *et al.*, 2007). The localized nature of holes in $LiFePO_4$ results in low electronic conductivity, and so conductive carbon coatings are commonly applied to ceramic $LiFePO_4$ particles to improve the overall electronic conductivity.

Summary

The layered structure has been intensely studied since even before the inception of the first practical Li^+ -ion battery cathode of $LiCoO_2$ in 1981. These investigations have led to a deep understanding of the structural nuances within these materials and how they affect their electronic structure, and finally their electrochemical performance. However, there are still underlying problems in many layered oxide cathode chemistries of interest and the layered structure provides an excellent framework for probing the electronic structure and phenomena of transition-metals in the solid-state. With their prominence in commercial lithium-ion batteries and the nature of the layered structure, it is likely that layered oxides will remain the dominant cathode choice for years to come. This article has served to introduce the important structural and electronic concepts required to understand the origin of the electrochemical behavior in lithium and sodium layered oxide cathodes with the hope that novel material compositions can be developed and investigated.

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In-Situ Spectroelectrochemistry in Li-O₂ Batteries

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Abstract

Aprotic lithium-oxygen battery has arguably become one of the most active new frontiers in energy storage systems in past decades. Aided by recent advances in highly sensitive *in situ* spectroelectrochemical techniques, a deepened mechanism understanding on the Li-O₂ chemistry during battery charge/discharge has been achieved, shedding light on potential optimization strategies to further improve the energy capabilities of Li-O₂ batteries. This article summarizes recent experimental efforts aimed at assessing the dynamic battery reactions at molecular level, including *in situ* electrochemical vibrational spectroscopies of Raman and FT-IR, and quantitative differential electrochemical mass spectroscopy approaches.

Key Points

- Spectroelectrochemical study on the battery reaction mechanisms.
- Identifying the chemical nature of reactive key intermediates and reaction interface.
- Correlating cells' capacity and rechargeability with the molecular level insights.

Introduction

Among various energy storage candidates, aprotic lithium-oxygen battery (LOB) is very attractive mainly due to its highest theoretical energy density ($\sim 3500 \text{ Wh kg}^{-1}$) among battery systems (Li and Chen, 2017; Kwak *et al.*, 2020). Despite its potential, there are yet many scientific and technical challenges, including low round-trip efficiency, poor cycle life, low power density, *etc.*, (Liu *et al.*, 2020). A deepened understanding on the reaction mechanism and the failure mechanism in LOBs is needed to address these challenges.

In nonaqueous LOBs, the anode is Li metal, the cathode is porous material with molecular oxygen acting as the reactant. For ideal LOBs, the battery reaction is $\text{O}_2 + 2\text{Li} \rightleftharpoons \text{Li}_2\text{O}_2$ where the core of cathode reaction is the generation and decomposition of lithium peroxide (Li_2O_2). In brief, O_2 is reduced on the cathode surface, then reacts with Li^+ to form Li_2O_2 during battery discharge (oxygen reduction reaction, ORR). During charge process, the generated Li_2O_2 is decomposed through oxygen evolution reaction (OER). (Lyu *et al.*, 2017) Currently, two kinds of generation mechanism are proposed: solution mechanism and surface mechanism. Namely, O_2 is firstly reduced by obtaining one electron to form a superoxide (O_2^- , LiO_2 , Eqs. 1–2). The superoxide is further reduced to Li_2O_2 undergoing a disproportionation reaction Eq. (3.1), namely the solution mechanism. The superoxide also can be reduced to Li_2O_2 by an electrochemical reduction at the electrode Eq. (3.2), resulting in a net two-electron charge transfer, namely the surface mechanism. In OER process, the decomposition mechanism of LiO_2 or Li_2O_2 , though still incompletely understood, are proposed to occur directly Eqs. (4)–(5) or to occur with a multi-step decomposition reaction.



Due to the complex solid/liquid/gas reaction interface, as well as the parasitic electrolyte decomposition side reactions occurring in the discharge/charge processes, the detailed reaction mechanism is much more complicated, which largely hinder the design of high-performance LOBs (Huang and Peng, 2019; Wang and Lu, 2020; Su *et al.*, 2022). To tackle these fundamental problems, different *in situ* spectroelectrochemical techniques have been developed, including but not limited to X-ray radiations like diffraction (XRD), photoelectron and absorption spectroscopies (XPS, XAS), surface-sensitive vibrational spectroscopies like Fourier transform Infrared (FT-IR), Raman and sum-frequency generation (SFG) spectroscopies, differential electrochemical mass spectroscopy (DEMS)

and so on (Lu *et al.*, 2013; Gittleson *et al.*, 2015; Cowan and Hardwick, 2019; Ganapathy *et al.*, 2014; Ge *et al.*, 2020b; Peng *et al.*, 2020; Ge *et al.*, 2020a). These *in situ* techniques can directly capture the dynamic molecular-level information at triple phase boundary during LOB operations, thus shed light on the reaction mechanism and/or failure mechanism.

Here in this article, we present an introduction on recent spectroelectrochemical approaches in LOBs, with representative Raman and FT-IR studies at the cathode/electrolyte interface and the *real-time* gaseous species quantification by DEMS. The fundamental aspects of each spectroscopic methodology, the operando apparatus setups and their applications in LOBs are overviewed accordingly. At last, the challenges and perspectives on coupling different spectroelectrochemical methods and converting the surface science investigations into real-world high-performance Li-O₂ batteries are proposed.

In Situ Electrochemical Raman Studies in LOBs

Raman vibrational spectroscopy provides critical information on the atomic environment and the local structure of molecules (Yang *et al.*, 2017). Under operando LOB working conditions, *in situ* electrochemical Raman spectroscopy is widely deployed to study the structural evolution information on the electrode/electrolyte interface during discharge/charge, especially for those transient states or air-sensitive intermediates. In principle, the vibrational Raman transition is sensitive to the polarizability change within chemical bonds, thus the transient species and discharge products (such as O₂^{•−}, LiO₂ and Li₂O₂) with O-O homopolar binding transitions can be effectively detected by *in situ* Raman technique. Nevertheless, since the intensity of Raman scattering is quite weak, surface-enhanced Raman spectroscopy (SERS) (Camden *et al.*, 2008; Zrimsek *et al.*, 2017) with magnitudes of higher surface sensitivity as enlarged by a roughened metal substrate like Au and Ag (Tian *et al.*, 2002) has been utilized for *in situ* LOB applications. Schematic of a two-electrode Raman spectroelectrochemical cell used in LOB is depicted in Fig. 1 (Gittleson *et al.*, 2015).

Identification of Reactive Oxygenated Species

Analyzing the reactive oxygen species in LOBs, such as superoxide (O₂^{•−}, LiO₂) and Li₂O₂ peroxide, helps to understand the battery's reaction mechanisms. In an early study, Peng *et al.* (2011) detected the reaction products during discharge-charge processes on an Au electrode with acetonitrile (CH₃CN) electrolyte using *in situ* SERS. As shown in Fig. 2(a), intermediate LiO₂ at ~1137 cm^{−1} was initially detected, followed by Li₂O₂ (at ~808 cm^{−1}) over the course of discharge. During charge process, both peaks were faded away gradually. Thereafter, more evidence of Li₂O₂ and oxygen-containing intermediates are identified based on the same technique but different operation conditions. (Qiao and Ye, 2016; Frith *et al.*, 2014; Radjenovic and Hardwick, 2018) For example, Qiao *et al.* (Qiao and Ye, 2016) monitored the formation/decomposition of Li₂O₂ in a DMSO-based electrolyte system (Fig. 2(b)), the Raman signal of O₂^{•−} in ionic liquids was successfully detected by Hardwick *et al.* (Radjenovic and Hardwick, 2018) Notably, superoxide formation in LOBs is affected by many factors, including the donor number (DN) of solvents, (Johnson *et al.*, 2014) cathode surface properties, (Yao *et al.*, 2019) operational parameters of batteries (current density, applied voltage), (Zhang *et al.*, 2016; Adams *et al.*, 2013). For instance, Johnson *et al.* (2014) discovered that high DN solvents like DMSO promotes O₂^{•−} generation, whereas low DN solvents like CH₃CN favors LiO₂ during discharge *via in situ* Raman spectroscopy. Peng *et al.* (Zhang *et al.*, 2016) investigated the effect of applied voltage on the formation of O₂^{•−}

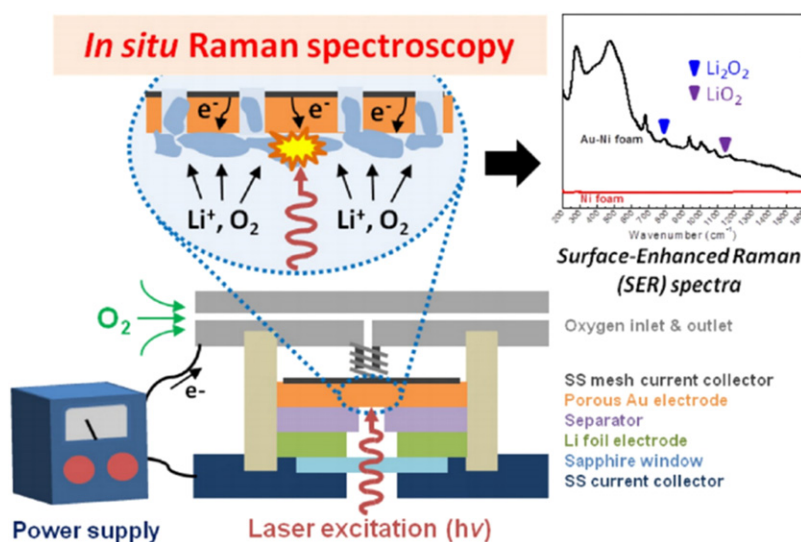


Fig. 1 *In situ* Li-O₂ cell schematic for Raman spectroscopy. Reprinted with permission from Gittleson, F.S., Yao, K.P.C., Kwabi, D.G., *et al.*, 2015. Raman spectroscopy in lithium-oxygen battery systems. ChemElectroChem 2, 1446–1457. Copyright 2015 Wiley-VCH.

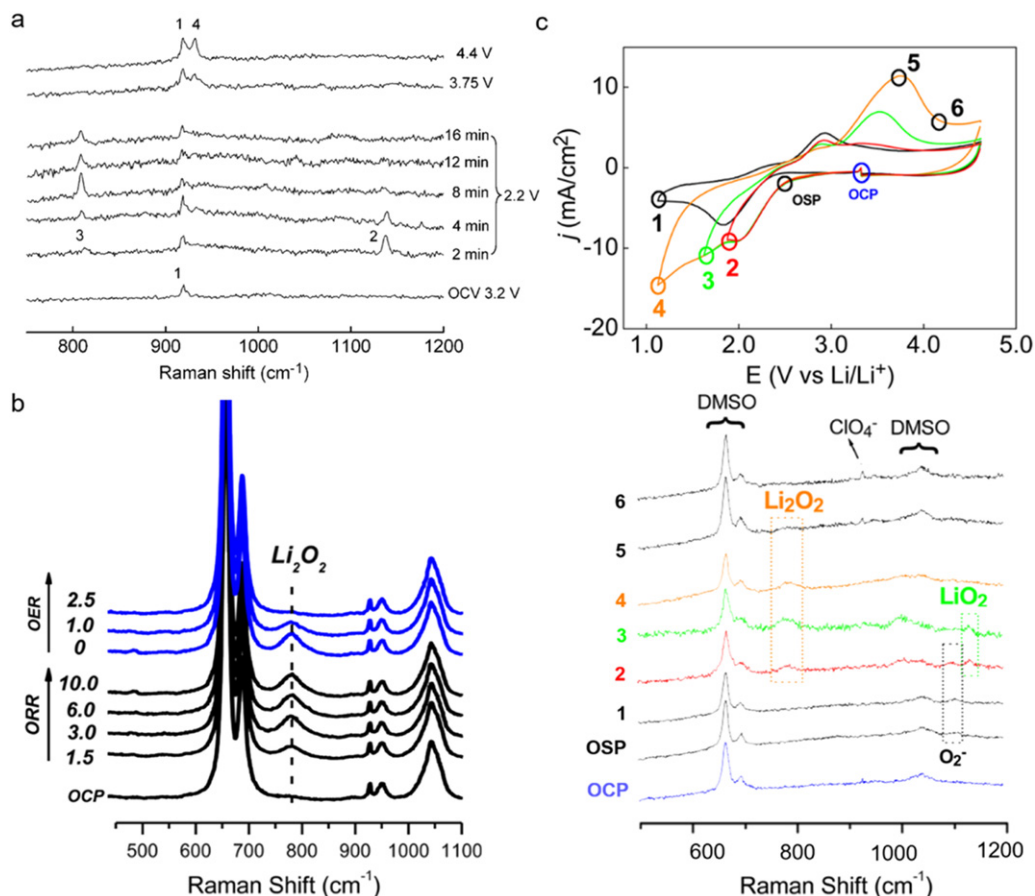


Fig. 2 *In situ* SER spectra on an Au electrode in different O₂-saturated electrolytes. (a) 0.1 M LiClO₄-CH₃CN. Peak assignments: 1 and 4 correspond to CH₃CN and ClO₄⁻, respectively; 2 and 4 correspond to the O-O stretch of LiO₂ and Li₂O₂, respectively. (b) 0.5 M LiClO₄-DMSO under different discharge/charge capacity during ORR/OER processes. (c) CVs on Au in 0.1 M TBAClO₄-DMSO (black) and in 0.1 M LiClO₄-DMSO with different cathodic cutoff potentials of 1.9 (red), 1.6 (green) and 1.1 V (orange) at a scan rate of 20 V s⁻¹ and the corresponding SERS spectra. Reprinted with permission from Peng, Z., Freunberger, S.A., Hardwick, L.J., *et al.*, 2011. Oxygen reactions in a non-aqueous Li⁺ electrolyte. *Angew. Chem. Int. Ed.* 50, 6351–6355. Qiao, Y., Ye, S., 2016. Spectroscopic investigation for oxygen reduction and evolution reactions with tetrathiafulvalene as a redox mediator in Li-O₂ battery. *J. Phys. Chem. C* 120, 15830–15845. Copyright 2016 American Chemical Society. Zhang, Y., Zhang, X., Wang, J., *et al.*, 2016. Potential-dependent generation of O₂⁻ and LiO₂ and their critical roles in O₂ reduction to Li₂O₂ in aprotic Li-O₂ batteries. *J. Phys. Chem. C* 120, 3690–3698. Copyright 2016 American Chemical Society.

and LiO₂ using *in situ* SERS. They found that O₂⁻ intermediate was formed above 1.9 V versus Li/Li⁺, while LiO₂ emerged at the low voltage during discharge in 0.1 M LiClO₄-DMSO electrolyte (Fig. 2(c)).

Notably, the signal intensities of Li₂O₂ and the Raman shift of superoxide are strongly dependent on its morphology and neighboring environments, respectively. Two primary morphologies of amorphous and toroidal Li₂O₂ are reported in LOBs. (Lin *et al.*, 2018; Li *et al.*, 2022a; Xing *et al.*, 2018) Siegel *et al.* (Tian *et al.*, 2014) found that amorphous Li₂O₂ exhibits a higher O-O vibrational frequency than that of toroidal Li₂O₂, and the former could be more easily detected by Raman spectroscopy. For superoxide species, its O-O bond vibration is largely affected by the microenvironment of solvent, cation and temperature (Sawyer and Valentine, 1981; Schwenke *et al.*, 2013). For instance, Rittner (1951) and Andrews (Andrews and Smardzewski, 1973) revealed its vibrational frequency increases with increasing polarization of cations, which could more easily attract electrons from the O-O anti-bond orbital as based on the ionic model. Moreover, Qiao and Ye (Yu and Ye, 2015) suggested that a low scan rate in DMSO-based electrolyte could be helpful to detect the O₂⁻ species.

Analysis of ORR/OER Pathways

The capacity of LOBs strongly depends on the LiO₂ chemistry and the relevant formation pathway of Li₂O₂ (Lyu *et al.*, 2017). For the surface pathway, generated LiO₂ during ORR is further reduced to film/disk-like Li₂O₂ on cathode surface *via* an electron transfer step, resulting in a quick cathode passivation that terminating the discharging with a “sudden death” of the cell Eq. (3.2). In contrast, for the solution pathway, generated LiO₂ gradually dissolves into the electrolyte and diffuses away from the electrode surface, leading to as a toroidal-shape Li₂O₂ deposition *via* a disproportionation step Eq. (3.1) and substantially increasing the discharge capacity (Johnson *et al.*, 2014; Aetukuri *et al.*, 2015).

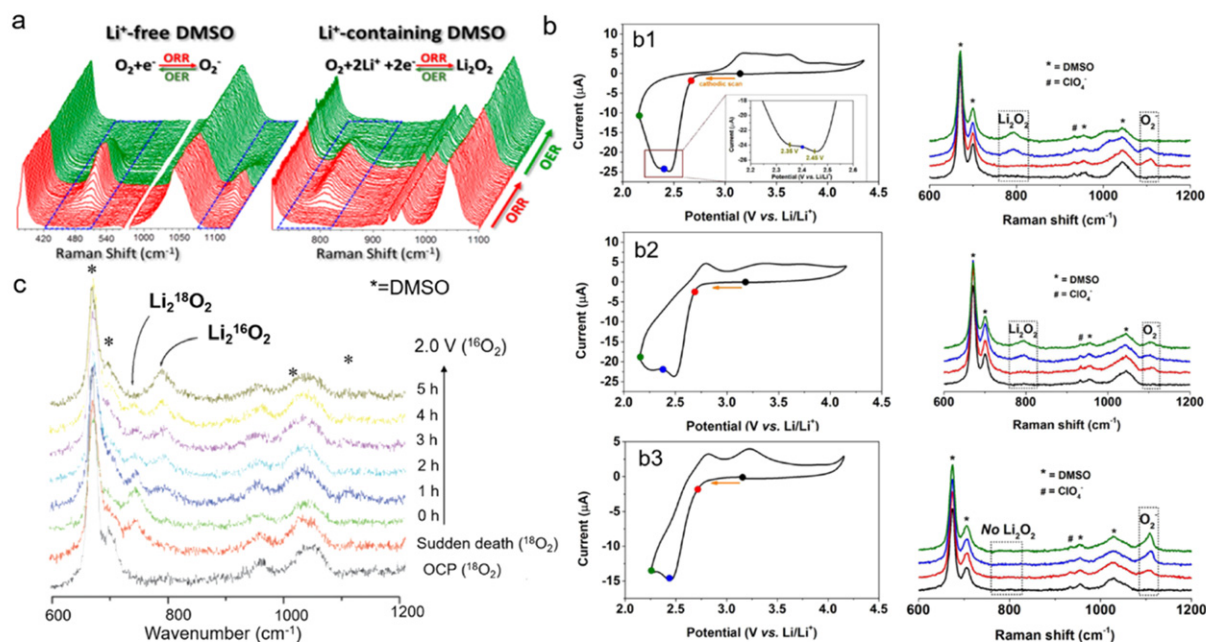


Fig. 3 (a) *In situ* SER spectra on an Au electrode in O₂ saturated 0.1 M TBAClO₄-DMSO (without Li⁺) and in O₂ saturated 0.1 M LiClO₄-DMSO during ORR/OER. (b) CV curves on an Au electrode in O₂ saturated 0.1 M LiClO₄-DMSO electrolytes with various contents of H₂O at scan rate of 50 mV s⁻¹ and corresponding SERS collected at different cathodic cutoff potentials: (b1) 0 M H₂O, (b2) 1 M H₂O, (b3) 10 M H₂O. (c) *In situ* SER spectra collected at OCP (black) and at end of passivation under ¹⁸O₂ (red) followed by other spectra at various times (0–5 h) of further discharging under ¹⁸O₂ at 2.0 V vs. Li/Li⁺. Reprinted with permission from Yu, Q., Ye, S., 2015. In Situ study of oxygen reduction in Dimethyl Sulfoxide (DMSO) solution: A fundamental study for development of the lithium–oxygen battery. *J. Phys. Chem. C* 119, 12236–12250. Copyright 2015 American Chemical Society. Ma, S., Wang, J., Huang, J., Zhou, Z., Peng, Z., 2018. Unveiling the complex effects of H₂O on discharge-recharge behaviors of aprotic lithium–O₂ batteries. *J. Phys. Chem. Lett.* 9, 3333–3339. Copyright 2018 American Chemical Society. Wang, J., Zhang, Y., Guo, L., Wang, E., Peng, Z., 2016. Identifying reactive sites and transport limitations of oxygen reactions in aprotic lithium–O₂ batteries at the stage of sudden death. *Angew. Chem. Int. Ed.* 55, 5201–5205. Copyright 2016 Wiley-VCH.

Early in this field, Bruce *et al.* pioneered *in situ* SERS characterizations on the time- and/or potential-dependence of LiO₂ and Li₂O₂ evolution in CH₃CN solution, proposing that O₂ was firstly reduced to LiO₂ and then converted into Li₂O₂ during ORR, whereas in OER process Li₂O₂ was directly decomposed to O₂ without the formation of LiO₂ intermediate (Fig. 2(a)) (Peng *et al.*, 2011, 2012). This Li₂O₂-mediated ORR/OER pathway was reinforced by follow-up studies in DMSO electrolyte (Peng *et al.*, 2012) and other groups (Aurbach *et al.*, 2016; Schroeder *et al.*, 2015). However, Taylor *et al.* (Gittleson *et al.*, 2014) came up with a different view on the role of LiO₂ using the same technique. In the 1st discharge, only the Raman feature of LiO₂ was observed at the absence of Li₂O₂, and the LiO₂ Raman signals gradually decreased in the 1st charge. Therefore, they concluded that the reversible formation/decomposition of LiO₂, rather than Li₂O₂, is the main active species for ORR and OER for LOBs in DMSO. On the other hand, *ex situ* Raman results confirmed the presence of Li₂O₂, which was probably arisen from the “late-stage” disproportionation of LiO₂ by a solution process diffused into bulk electrolyte rather than a surface redox reaction (Zhai *et al.*, 2014). Therefore, to obtain more reliable reaction mechanism information, comprehensive spectroelectrochemical techniques need to be adopted.

Thereafter, *in situ* SERS has been widely deployed to distinguish these two pathways and to identify the factors influencing the reaction pathway in LOBs, including but not limited to solvents, cations, redox mediators (RMs) and H₂O impurity. Johnson *et al.* (2014) reported the effect of solvent on ORR process using *in situ* SERS, *i.e.*, through a solution-based pathway (O₂⁻) in high DN solvents like 1-methylimidazole (Me-Im) and DMSO, or through a surface-based pathway (LiO₂) in low DN solvents like dimethoxyethane (DME) and CH₃CN. (Aetukuri *et al.*, 2015; Aurbach *et al.*, 2016; Ye *et al.*; Yu and Ye, 2015) compared the SERS feature of two different cations (TBA⁺ and Li⁺) in DMSO-based electrolyte (Fig. 3(a)). In TBA⁺-containing DMSO, two sets of Raman peaks at 1105 and 490 cm⁻¹ were observed, which were attributed to the O–O stretching and Au–O stretching modes for adsorbed superoxide on Au surface, respectively. Based on this Raman feature, they concluded that the ORR/OER processes involve a one-electron transfer ($O_2 + e^- \rightleftharpoons O_2^-$) in Li⁺-free electrolyte. In contrast, within the Li⁺-containing DMSO, Li₂O₂ species was clearly identified at 788 cm⁻¹, indicating a two-electron transfer reaction ($O_2 + 2Li^+ + 2e^- \rightleftharpoons Li_2O_2$) pathway.

Apart from high DN solvents, using additives with high acceptor number (AN) like H₂O (AN = 55) or with high DN anions like NO₃⁻ were reported to improve the battery capacity by promoting a solution-driven ORR mechanism (Li *et al.*, 2022b; Deng *et al.*, 2019; Aetukuri *et al.*, 2015). For example, Peng *et al.* (Ma *et al.*, 2018) studied the impact of H₂O content in O₂-saturated 0.1 M LiClO₄-DMSO. As shown in Fig. 3(b), at the absence of H₂O (b1), only adsorbed superoxide species (*O₂⁻) was observed at the ORR onset potential (red line), implying that Li₂O₂ forms at this low overpotential region steered by a sluggish solution-mediated

disproportionation mechanism *via* stable *O_2^- intermediate. At high overpotentials, Li_2O_2 species accompanying with *O_2^- appears on the SERS curve (blue line) *via* a fast surface-mediated mechanism. Then, at even negative potential (olive curve), only Li_2O_2 signature is observed on SERS as due to the rapid transformation of absorbed *O_2^- into surface- Li_2O_2 . At the presence of H_2O , the *O_2^- species could be persistently detected on the surface of Au electrode even at the highest overpotential (olive curve), thus rationalizing that H_2O intrusion suppresses the Li_2O_2 surface-mediated mechanism even at high overpotentials but promotes the solution-mediated growth mechanism. Nevertheless, it should be noted that the presence of trace H_2O could potentially react with superoxide or peroxide, generating more active singlet oxygen ($^1\text{O}_2$) and leading to more parasitic reaction products (Mahne *et al.*, 2017). The involvement of H_2O in LOBs therefore requires extra caution.

However, the increased solvation of superoxide from enhanced solution pathway could extend the lifetime of superoxide and the generation of $^1\text{O}_2$ from LiO_2 disproportionation, giving rise to additional parasitic processes (Khetan *et al.*, 2015; Kwabi *et al.*, 2014; Mourad *et al.*, 2019). Targeted on this issue, RMs, as soluble catalysts, have been proposed to circumvent the trade-off between capacity and rechargeability in solution pathway. (Liu *et al.*, 2018; Vivek *et al.*, 2019; Qiao and Ye, 2016; Gao *et al.*, 2016) introduced the reduction mediator of 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) and found that the $\text{LiDBBQO}_{2(\text{sol})}$ intermediate promotes the formation of solution phase Li_2O_2 in LOBs. The $\text{LiDBBQO}_{2(\text{sol})}$ intermediate is more stable than soluble LiO_2 , mitigating the parasitic reactions. More recently, Vivek *et al.* (2019) deployed *in situ* SERS and online electrochemical mass spectrometry investigations to further verify the promotion effect of DBBQ on the solution-mediated $2e^-$ ORR pathway in LOBs. Similarly, *via* a combined *in situ* SERS, online DEMS and DFT approach, Zhao *et al.* (2022) proposed an anthraquinone (AQ) enhanced solution-mediated ORR pathway based on the direct spectroscopic evidence of LiAQ and LiAQO_2 intermediates observed in the discharge of LOBs.

Analysis of Reaction Interfaces

In LOBs, the cathodic reactions may take place at the cathode- Li_2O_2 , the Li_2O_2 -electrolyte or the cathode-electrolyte interfaces. Each kind of reaction interface involves a distinct reaction route that varying battery performance. Bitter controversies are noted regarding the reactive interface assessment.

Wang *et al.* (2016) carried out an *in situ* SERS study of ORR/OER on Au within 0.1 M LiClO_4 -DMSO using $^{18}\text{O}_2$ for pre-passivation and $^{16}\text{O}_2$ for further discharging (Fig. 3(c)). The cell was firstly discharged to the state of “sudden death” under the atmosphere of $^{18}\text{O}_2$ at 100 $\mu\text{A cm}^{-2}$, where the discharge product of $\text{Li}_2^{18}\text{O}_2$ was detected at 745 cm^{-1} (^{18}O - ^{18}O). Subsequently, $^{18}\text{O}_2$ was switched to $^{16}\text{O}_2$ purge for 10 min at a holding potential of 2.4 V, for which $\text{Li}_2^{18}\text{O}_2$ still dominates on Au. Upon the following discharge at 2.0 V under $^{16}\text{O}_2$ atmosphere, characteristic $\text{Li}_2^{16}\text{O}_2$ band was found at 790 cm^{-1} with increasing band intensity as a function of discharging time till the complete substitution of $\text{Li}_2^{18}\text{O}_2$. This displacement as revealed by surface-sensitive SERS technique suggests that the reactive sites of ORR are located at the AuLi_2O_2 interface, and in return provides evidence that at the stage of sudden death ORR is limited by the electron transport instead of Li^+ or O_2 transport. Furthermore, this AuLi_2O_2 interface has also been assigned at the active sites for OER as derived from *in situ* SERS and isotope labeling results. Though similar conclusions have been reinforced by other reports with either SERS or other spectroelectrochemical techniques, (Peng *et al.*, 2018; Zhong *et al.*, 2013; Kushima *et al.*, 2015; He *et al.*, 2018; Tomita *et al.*, 2020) conflicting views still prevail in literature. (Zheng *et al.*, 2014; Wang and Lu, 2019) For example, Lu *et al.* (Wang and Lu, 2019) studied the reaction interface in a regular Li-O₂ cell using time-of-flight secondary ion mass spectroscopy (TOF-SIMS), DMES, and isotope-labeling techniques, suggesting that ORR/OER take place at the Li_2O_2 /electrolyte interface (see Section “Isotope Labeling” of DEMS discussion for details). Therefore, a conclusive picture on the reactive interface yet relies on the multiple complementary *in situ* spectroelectrochemical techniques and operando characterizations in the future.

In Situ FT-IR Applications in LOBs

As discussed above, *in situ* Raman technique is a powerful nondestructive tool to probe the electrode/electrolyte interface and to capture the reaction intermediates information (*i.e.*, *O_2^- , LiO_2 and Li_2O_2) with significant polarizability change. As a complementary vibrational spectroscopy, FT-IR is another surface sensitive technique to probe the reactive intermediates and liquid phase products involved in LOBs operation. The IR absorption are typically sensitive to the dipole components transition perpendicular to the electrode surface, giving rise to six orders of magnitude higher signal as compared to that from Raman scattering, providing valuable information on reaction mechanism and the electrolyte decomposition mechanism. (Cowan and Hardwick, 2019).

To explore the electrode/electrolyte interface, two kinds of *in situ* FT-IR spectroelectrochemical setups have been developed at high signal-to-noise ratio, *i.e.*, the Kretschmann-mode internal attenuated total reflection (ATR) cell and the external reflection cell (Fig. 4). (Chen *et al.*, 2021; Ye *et al.*, 2016) In ATR mode, a thin metal film was deposited onto an IR transparent prism with high refractive index (*i.e.*, ZnSe, Si, Ge and diamond) serving as the working electrode. The IR beam is focused at the interface from the back of the electrode (through the prism) without passing through the solution, gets totally reflected at the electrode/electrolyte interface and generates evanescent wave to penetrate the island metal film electrode into electrolyte within a total few hundred nanometers depth. As a result, an unlimited solution layer can be used in ATR mode, and this configuration is highly sensitive in monitoring the adsorbed species at electrode surfaces (known as surface enhanced infrared absorption, SEIRA effect (Osawa, 1997)) without the interference from bulk solution. In external reflection mode, the working electrode is placed in close contact to the IR window to

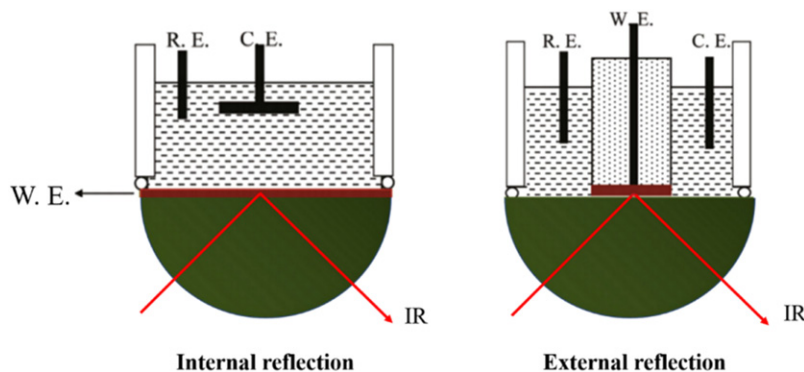


Fig. 4 Schematic presentations of *in situ* FT-IR cell using either internal attenuated total reflection or external reflection configurations. Reprinted with permission from Ye, J.Y., Jiang, Y.X., Sheng, T., Sun, S.G., 2016. In-situ FTIR spectroscopic studies of electrocatalytic reactions and processes. *Nano Energy* 29, 414–427. Copyright 2016 Elsevier.

form a thin electrolyte layer (few $\sim \mu\text{m}$ in thickness). Though both surface adsorbates and products could be potentially detected, this external reflection configuration is more sensitive to solution phase species generated/consumed during LOBs operation.

Analysis of ORR Pathway

Exploring the chemical identity of oxygenated intermediates helps understand the ORR/OER mechanism in LOBs. Since the O-O homopolar binding transitions in superoxides and peroxides are Raman active, IR spectroscopy could provide additional information on the $\text{M}_x\text{-O}_2$ species assignment with active dipole moments change. In 2017, Hardwick's group (Vivek *et al.*, 2017) carried out *in situ* ATR-SEIRAS investigation on the discharge products in LOB using an Au-coated ZnSe as both the working electrode and the IR window (Fig. 5(a)). Combined with theoretical wavenumber calculations, they found molecular metal superoxide of LiO_2 and peroxide of Li_2O_2 are IR-active and easily detected within electrolytes containing high DN solvent like DMSO. However, no prominent IR peaks of these oxygenated species were detected in electrolytes composed of low DN solvent like Li^+ -MeCN. Based on these ATR-SEIRAS results, they're able to distinguish the solution-mediated reaction pathway from surface-reaction mechanism. This methodology has also been successfully extended to identify other reactive complexes like duroquinone- Li-O_2^- in a quinone-based electrolyte (Zhu *et al.*, 2018).

Analysis of Electrolyte Decomposition Side Reactions

In nonaqueous LOBs, the organic solvents more or less suffer from the attack of active oxygenated species (superoxide, peroxide intermediates or $^1\text{O}_2$), giving rise to irreversible decomposition side reactions (Lai *et al.*, 2020; Mourad *et al.*, 2019) and ubiquitous capacity fading. Therefore, understanding the mechanistic details of oxygenates induced dynamic solvent degradation at the molecular level is crucial in developing stable electrolytes for LOBs.

Organic carbonates such as propylene carbonate (PC), were initially deployed as the electrolyte solvent in LOBs, where its irreversible decomposition and oxidation to Li_2CO_3 and RO-(C=O)-OLi rather than Li_2O_2 were observed (Freunberger *et al.*, 2011; Xu *et al.*, 2011b) by *ex situ* spectroscopic characterizations. Although the degradation of organic carbonates has been reported in LOBs, the detailed decomposition route is not clearly defined at molecular level. In 2016, Hardwick *et al.* (Vivek *et al.*, 2016) applied *in situ* ATR-SEIRAS to track the PC decomposition mechanism in either Li^+ -free 0.1 M $\text{TEAClO}_4\text{-PC}$ (Fig. 5(b)) or 0.1 M $\text{LiClO}_4\text{-PC}$ electrolyte (Fig. 5(c)). At absence of Li^+ cation, only the PC and TEA^+ vibrational bands were observed, indicating that no new species are formed at the interface. In contrast, within Li^+ -containing electrolyte, the loss of PC was clearly observed from the upward going bands of $\sim 1813\text{ cm}^{-1}$ for $\nu_{\text{C=O}}$, $1055\text{--}2289\text{ cm}^{-1}$ for $\nu_{\text{s,C-O}}$ and $\nu_{\text{s,C-C}}$ stretching at the interface, accompanied with the strong downward bands at $1315\text{--}1676\text{ cm}^{-1}$ indicative for the formation of ring-opened carbonate species, ROCO_2Li (Fig. 5(d)). Combining with DFT calculation, they proposed that a superoxide-induced ring opening in PC solvent by nucleophilic attack is favored only in the presence of alkali metal cation, rather than organic cation. More recently, Ye and co-workers deployed several different spectroelectrochemical methods of SFG, SERS and UV-vis absorption spectroscopy to probe the PC decomposition with or without Li^+ cation. (Peng *et al.*, 2020) They revealed the ring opening reaction of PC regardless the presence of Li^+ , *i.e.*, peroxodicarbonate of $\text{C}_2\text{O}_6^{2-}$ as the main product in Li^+ -free electrolyte while lithium carbonate product in Li^+ -PC.

DMSO is another widely used electrolyte in LOBs with a better cycling stability compared to PC. (Schroeder *et al.*, 2015; Calvo *et al.*; Mozzhukhina *et al.*, 2013) systematically investigated the stability of DMSO-based electrolyte on an Au electrode using *in situ* subtractive normalized Fourier transform infrared spectroscopy (SNIFTIRS) with external reflection mode. The generation of DMSO_2 (1142- and 1295-cm^{-1} peaks) and the consumption of H_2O ($\sim 3500\text{ cm}^{-1}$) were noticed above 4.2 V (compared to the ring opening reaction of PC at $\sim 2.4\text{ V}$), regardless the operation conditions of gas atmospheres (Ar or O_2) and cations (with or without Li^+) in electrolyte (Fig. 6(a)). As a result, they speculated that the trace amount of H_2O , rather than O_2^- , triggers the

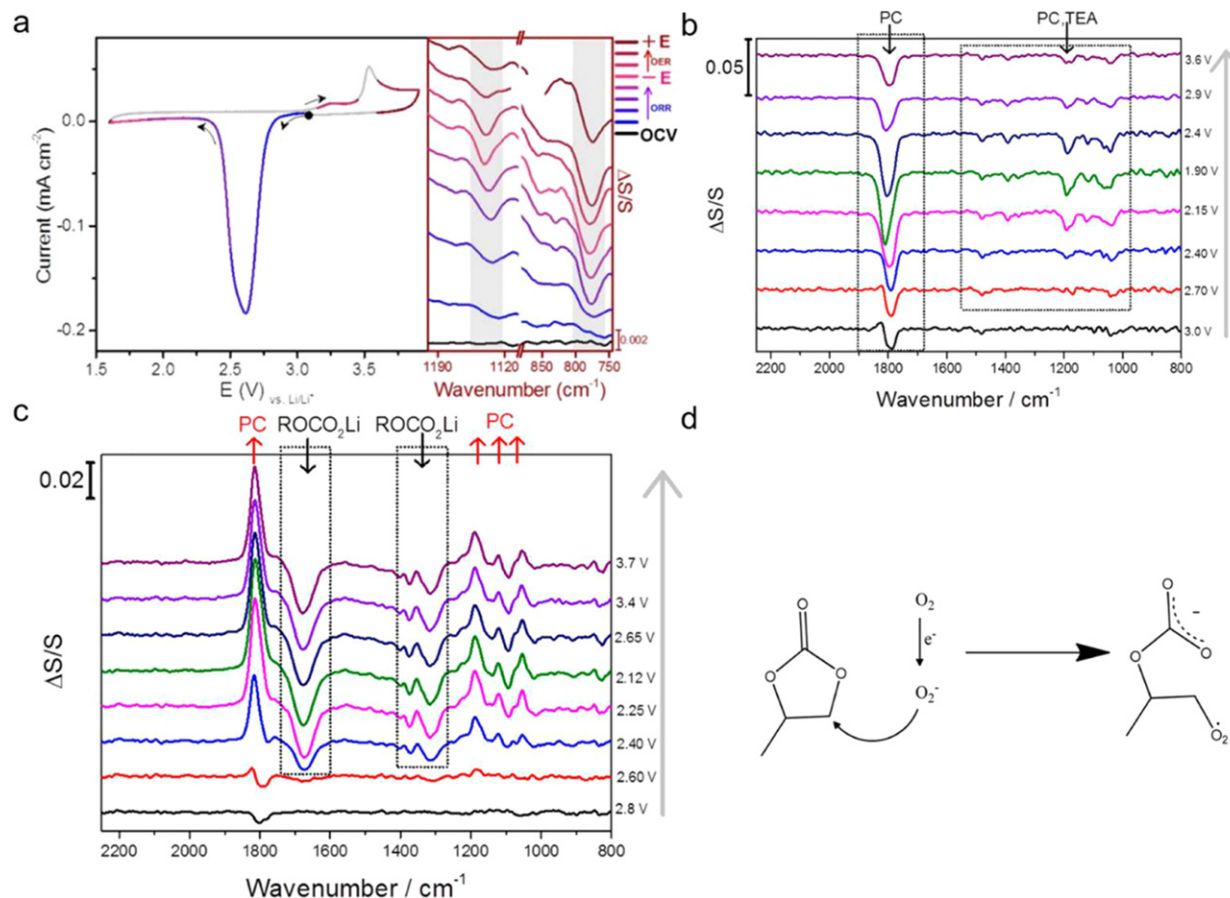


Fig. 5 (a) CV of ORR/OER at 10 mV s⁻¹ scan rate in O₂ saturated 0.1 M LiOTf-DMSO on an Au electrode and corresponding *in situ* ATR-SEIRAS. (b and c) *in situ* ATR-SEIRA spectra on an Au electrode in O₂ saturated 0.1 M TEAClO₄-PC and in O₂ saturated 0.1 M LiClO₄-PC, respectively. (d) Schematic diagram of superoxide induced ring opening in PC. Reprinted with permission from Vivek, J.P., Berry, N.G., Zou, J.L., Nichols, R.J., Hardwick, L.J., 2017. In Situ surface-enhanced infrared spectroscopy to identify oxygen reduction products in nonaqueous metal-oxygen batteries. *J. Phys. Chem. C* 121, 19657–19667. Copyright 2017 American Chemical Society. Vivek, J.P., Berry, N., Papageorgiou, G., Nichols, R.J., Hardwick, L.J., 2016. Mechanistic insight into the superoxide induced ring opening in propylene carbonate based electrolytes using *in situ* surface-enhanced infrared spectroscopy. *J. Am. Chem. Soc.* 138, 3745–3751. Copyright 2016 American Chemical Society.

decomposition of DMSO solvent above 4.2 V, leading to the side products of DMSO₂. The authors explained that DMSO could undertake against nucleophilic attack by the electrogenerated superoxide radical anion during a short-time SNIFTIRS measurements but react with H₂O molecules to form DMSO₂ at high potentials. Other side products like Li₂CO₃ and CO₂ were also detected by various *in situ* and *ex situ* characterizations in DMSO-based electrolyte *via* a long term nucleophilic attack from superoxide (Peng *et al.*, 2012; Mozhzhukhina *et al.*, 2017a).

Ether-based solvents are generally stable against nucleophilic attack of superoxide and proven to be the most appropriate class of solvents in LOBs. Ye *et al.* (Ge *et al.*, 2022) studied the cation effect on the stability of tetraglyme (TEGDME)-based electrolyte *via* a combined spectroelectrochemical approach of *in situ* SFG, SNIFTIRS and SERS. As shown in Figs. 6(b)-(c), no tetraglyme decomposition products (like acetate and/or formate species at 1609 cm⁻¹) were observed at the presence of Li⁺, confirming the stability of TEGDME under the operation conditions of LOBs. Comprehensive *in situ* SFG and SERS studies further confirmed the solution phase O₂⁻ boosts the decomposition of TEGDME at the absence of Li⁺, in agreement with earlier studies (Zhang *et al.*, 2017). Besides, Horwitz *et al.* (2020) carried out *in situ* SNIFTIRS investigations on TEGDME-based electrolyte, suggesting that a solvent with stronger ionic association strength for Li⁺ and/or with a shorter glymes is more stable in LOBs. Similarly, the stability of other organic solvents in LOBs also were investigated using *in situ* FTIR technique (Mozhzhukhina *et al.*, 2017b).

In summary, both *in situ* SERS and FT-IR techniques provide valuable information on the dynamic evolution of key intermediates and interfacial species during LOBs operation at molecular level. For the LiO₂ chemistry and Li₂O₂ generation pathway studies, SERS probes the O-O homopolar binding transitions in superoxides and peroxides while FT-IR captures the complementary dipole moments change in M_x-O₂ species, in together aiding to the solid assignment of reactive oxygenated intermediates in ORR/OER. Moreover, the mechanism study on electrolyte decomposition and other solution-mediated parasitic reactions by *in situ* FT-IR spectroscopy could shed light on the development of more stable electrolyte in the future.

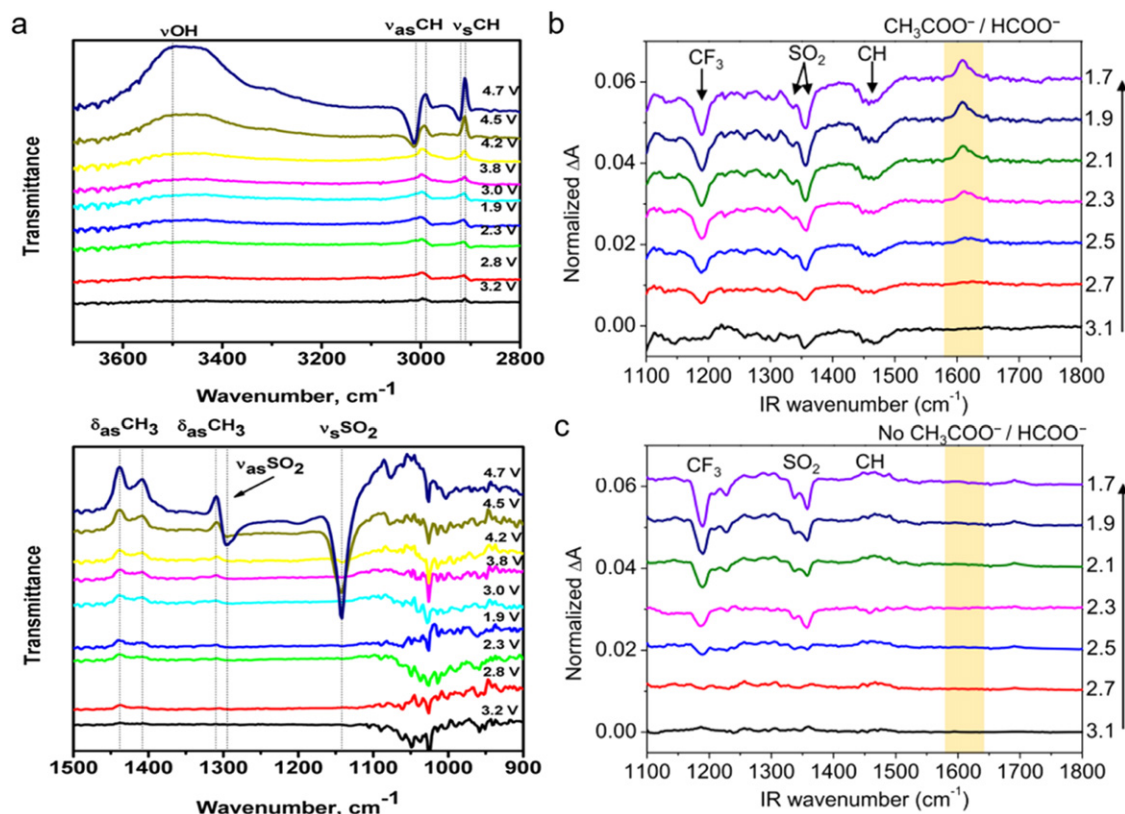


Fig. 6 *In situ* SNIFTIRS on an Au electrode in different O₂-saturated electrolytes. (a) 0.1 M LiPF₆/DMSO. (b) 0.1 M TBATFSI/TEGDME. (c) 0.1 M LiTFSI/TEGDME. Reprinted with permission from Mozhzhukhina, N., Méndez De Leo, L.P., Calvo, E.J., 2013. Infrared spectroscopy studies on stability of dimethyl sulfoxide for application in a Li-Air battery. *J. Phys. Chem. C* 117, 18375–18380. Copyright 2013 American Chemical Society. Ge, A., Nagai, R., Xu, C., *et al.*, 2022. Unraveling the unstable nature of tetraglyme-based electrolytes toward superoxide and the inhibitory effect of lithium ions by using *in situ* vibrational spectroscopies. *J. Phys. Chem. C* 126, 2980–2989. Copyright 2022 American Chemical Society.

DEMS Applications in LOBs

In addition to the above adsorbates and interfacial species investigations by surface-sensitive vibrational spectroscopy, examining the gaseous species evolution during discharge/charge processes at real-time is of equal importance for clarifying the reaction mechanisms in LOBs. Compared to gas chromatography, online DEMS is a more powerful technique for volatile species quantification at higher temporal resolution (Zhao and Peng, 2019; Wang *et al.*, 2017; Ye *et al.*, 2022).

DEMS setup was initially introduced by Heitbaum *et al.* (Wolter and Heitbaum, 1984) in 1984, consisting of a multistage differential pumped vacuum system, a electrochemical cell and a piece of microporous PTFE membrane sitting in between to separate liquid from pervaporated products. The gaseous species are firstly ionized by an ion source, and the generated fragments are captured by a detector after the journey through a quadrupole rod applied with high radio frequency voltage. No column separation process is needed and the recorded ion mass current or partial pressure is proportional to the relative concentration of specific m/z , making this technique suitable for real time electrochemical analysis as well as the mechanism study with isotope labeling. (Yan *et al.*, 2021) By using an classic membrane-inlet DEMS setup, Baltruschat *et al.* (Bawol *et al.*, 2018) reported a thin-layer DEMS flow cell configuration using an Au-coated microporous PTFE as both the pervaporation membrane and the working electrode (Fig. 7(a)). This configuration exhibits a high electrode surface area to electrolyte volume ratio that closer to LOB operation conditions, enabling a real-time detection of volatile species (such as $m/z = 32$ for O₂ and $m/z = 44$ for CO₂) formed during the OER and/or electrolyte decomposition side reaction. McCloskey *et al.* (2012b) came up with a Swagelok-type DEMS cell design (Fig. 7(b)) consisting of Li metal anode, Celgard 2500 separators, a carbon cathode, and a small headspace of 40–60 μ L. Furthermore, by using a switchable valve, 2 operation modes have been demonstrated, *i.e.*, one for products accumulation in the headspace and the other for products transfer to mass spectrometer by carrier gas *via* a capillary tube. This cell design exhibits a low detection limit less than 1 ppm while at the sacrifice of temporal resolution. Toward a balance improved temporal resolution and detection sensitivity, as well as to avoid the potential quantitation errors by gases dissolution in electrolyte or trapping in cell, Peng *et al.* (2012) designed a cell stack with spiral-type flow field (Fig. 7(c)). In this setup, working electrode like a nanoporous Au mesh is placed at the cell bottom, with Li metal serving as the counter and/or reference electrode and glass fiber as the separator material. During charge/discharge, a gentle mass-controlled carrier gas is to be purged through the spiral-type flow field below the working electrode, sampling the gaseous effluent into mass spectrometer at real time.

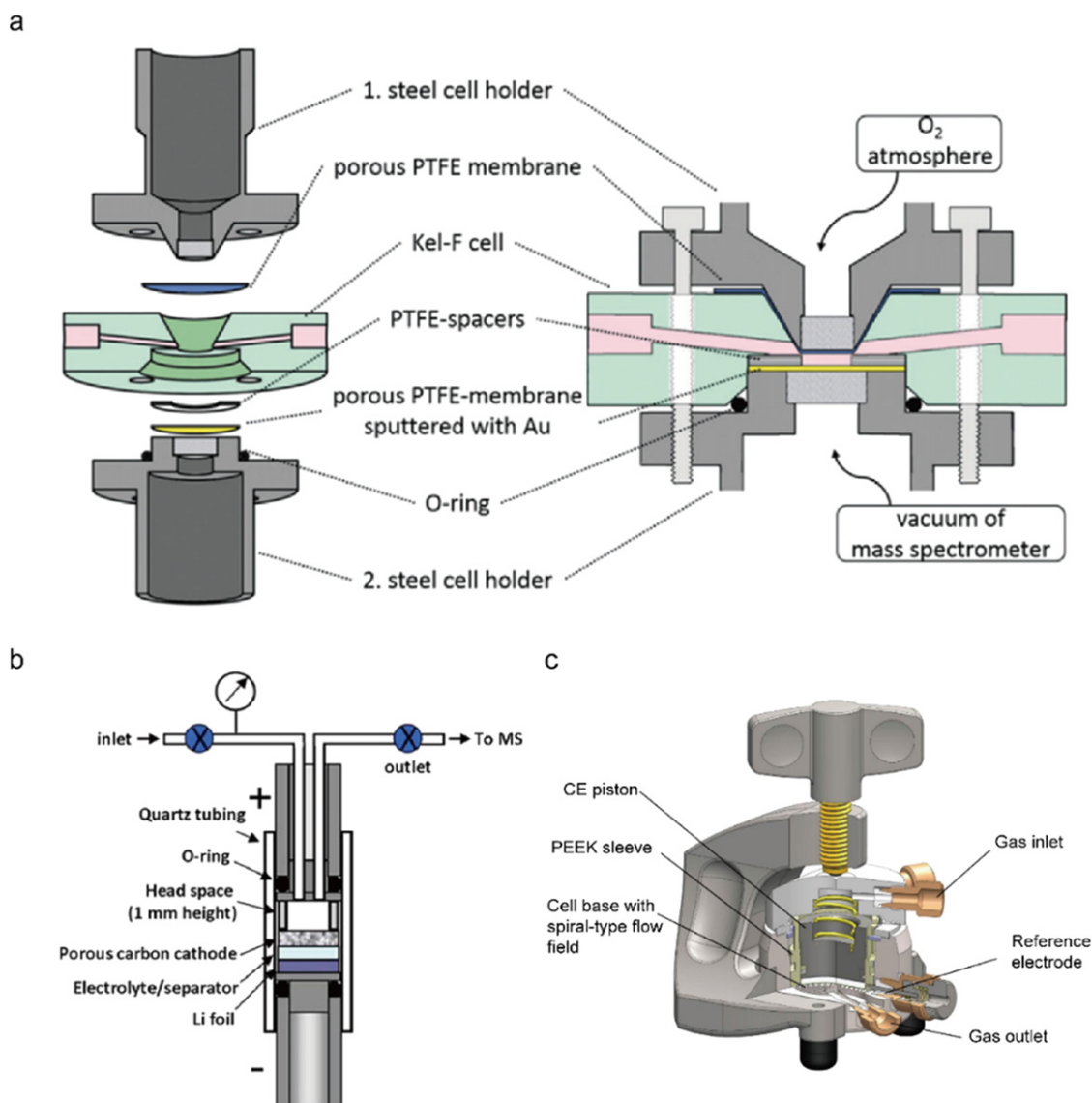


Fig. 7 Representative DEMS setups for LOB investigation. (a) membrane-inlet thin-layer DEMS flow cell design. (b) headspace DEMS cell design with switchable sampling valve. (c) DEMS cell design with spiral-type flow field. Reprinted with permission from Bawol, P.P., Reinsberg, P., Bondue, C.J., *et al.*, 2018. A new thin layer cell for battery related DEMS-experiments: The activity of redox mediators in the Li-O₂ cell. *Phys. Chem. Chem. Phys.* 20, 21447–21456. Copyright 2018 Royal Society of Chemistry. McCloskey, B.D., Scheffler, R., Speidel, A., Girishkumar, G., Luntz, A.C., 2012b. On the mechanism of nonaqueous Li-O₂ electrochemistry on C and its kinetic overpotentials: some implications for Li-Air batteries. *J. Phys. Chem. C* 116, 23897–23905. Copyright 2012 Royal Society of Chemistry. Peng, Z., Freunberger, S.A., Chen, Y., Bruce, P.G., 2012. A reversible and higher-rate Li-O₂ Battery *Science* 337, 563–566. Copyright 2012 AAAS.

Quantitative Analysis of O₂ Generation and Consumption

In LOBs, quantitative measurement of the Coulombic efficiency (e^-/O_2) and the O₂ recovery efficiency (OER/ORR) during electrochemical charge and discharge process is of great importance for the battery rechargeability evaluation. *In situ* DEMS is a powerful tool to quantitatively measure the consumed and generated O₂ content during LOBs operation, thus providing real time information for the chemical rechargeability assessment of Li-O₂ cells.

Li₂O₂-mediated $2e^-/\text{O}_2$ OER/ORR process are presumed as the dominant reaction pathway in aprotic cells (Girishkumar *et al.*, 2010; Chen *et al.*, 2013; Ottakam Thotiyl *et al.*, 2013; Asadi *et al.*, 2018). As shown in Fig. 8(a), the amount of O₂ consumption and evolution during linear sweep voltammetry have been successfully tracked by *in situ* DEMS on a nanoporous Au cathode using the setup described in Fig. 7(c) (Peng *et al.*, 2012). During discharge, the consumed O₂ follows the cell current at a charge-to-mass ratio of $2e^-/\text{O}_2$, suggestive the high purity of Li₂O₂ formation. Moreover, through the synergetic approach of FT-IR, SERS NMR and DEMS over the collection of up to 100 cycles, Bruce *et al.* demonstrate the cell rechargeability *via* reversible formation/decomposition of Li₂O₂. Luntz and co-workers combined Coulometry with O₂ quantification with a similar DEMS approach, but arguing

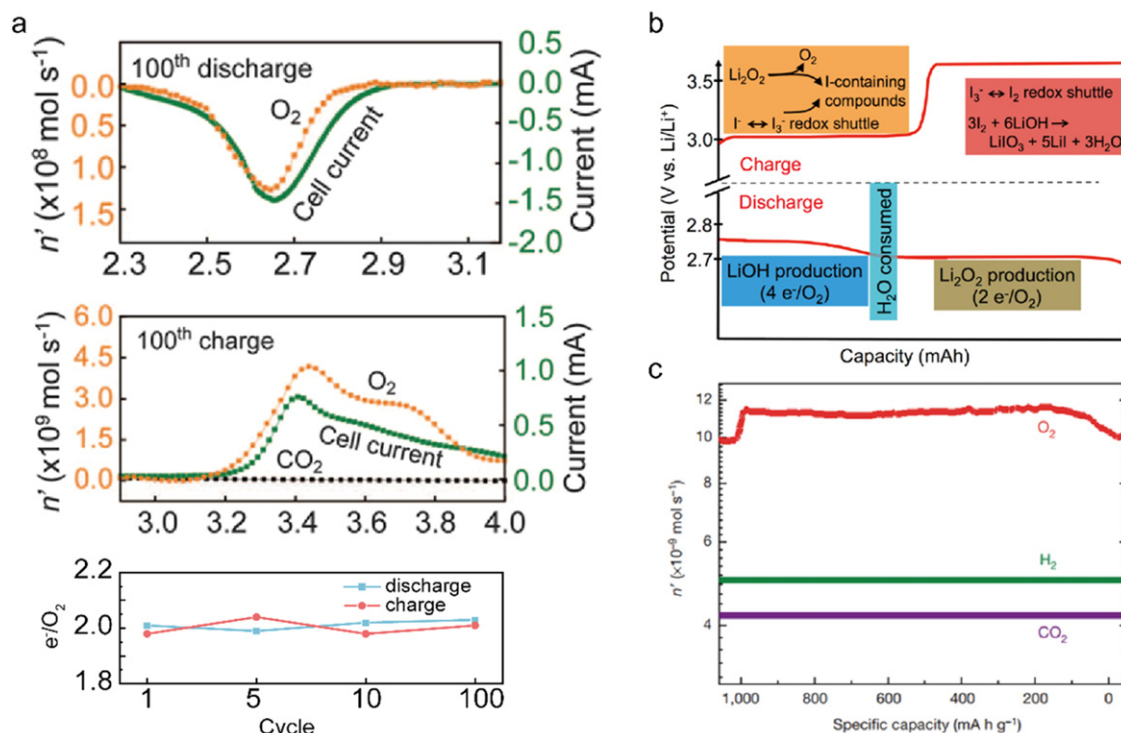


Fig. 8 Quantitative Analysis of LOBs by DEMS. (a) $m/z = 32$ signal (O_2) obtained by DEMS and analysis of e^-/O_2 during 100th charge/discharge. (b) switch of $4e^-$ oxygen reduction to LiOH and $2e^-$ to Li_2O_2 on discharge with addition of LiI and H_2O in LOBs. (c) DEMS results showing O_2 , H_2 and CO_2 gases released rate during the charging process with Ir-rGO cathode LOBs. Reprinted with permission from Peng, Z., Freunberger, S.A., Chen, Y., Bruce, P. G., 2012. A reversible and higher-rate Li-O₂ Battery Science 337, 563–566. Copyright 2012 AAAS. Burke, C.M., Black, R., Kochetkov, I.R., *et al.*, 2016. Implications of $4 e^-$ oxygen reduction via iodide redox mediation in Li-O₂ batteries. ACS Energy Lett. 1, 747–756. Copyright 2016 American Chemical Society. Lu, J., Lee, Y.J., Luo, X., *et al.*, 2016. A lithium-oxygen battery based on lithium superoxide. Nature 529, 377–382. Copyright 2016 Springer Nature.

that the cell rechargeability in various electrolytes is limited both by chemical reaction of Li_2O_2 with the solvent and by electrochemical oxidation reactions during charging at potentials below the onset of electrolyte oxidation on an inert electrode, imposing the stringent conditions on the liquid electrolyte in LOBs (McCloskey *et al.*, 2012a).

In 2015, Gray and co-workers disclosed a LiOH -mediated $4e^-/\text{O}_2$ cycling in LOB, using a reduced graphene oxide electrode, the additive LiI , and the dimethoxyethane solvent to reversibly form and remove crystalline LiOH with particle sizes larger than 15 micrometers during discharge and charge. (Liu *et al.*, 2015) Thereafter, McCloskey *et al.* quantitatively analyzed the influence of LiI and H_2O on the electrochemistry in a common LOB employing an a carbon cathode and a dimethoxyethane-based electrolyte containing 0.25 M LiTFSI , 0.05 M LiI and ~ 2000 ppm H_2O (Burke *et al.*, 2016). Through a combined iodometric titration, ^{18}O isotope labeling and DEMS quantitation (Fig. 8(b)), they concluded that the addition of LiI and H_2O promotes efficient $4e^-$ oxygen reduction to LiOH on discharge. However, LiOH is not able to reversibly be oxidized back to O_2 on charge, where instead a complicated mix of redox shuttling and side reactions is observed.

Similarly, Lu *et al.* (2016) reported a stable LiO_2 -mediated $1e^-/\text{O}_2$ cycling in contrast to standard Li_2O_2 -pathway in LOBs, using a reduced graphene oxide cathode with added iridium nanoparticles (Ir-rGO). DEMS measurements were carried out to quantify the generated and consumed O_2 content. Fig. 8(c) shows an average O_2 formation rate of $1.3 \times 10^{-9} \text{ mol s}^{-1}$ with negligible amounts of CO_2 and H_2 gases, resulting in an e^-/O_2 ratio of 1.00 in the low battery charge voltage. Similarly, an e^-/O_2 ratio of 1.02 is noted during discharge, in together confirming the cell rechargeability via LiO_2 -mediated $1e^-/\text{O}_2$ pathway. This route has been further verified by follow-up *in situ* transmission electron microscopy (Luo *et al.*, 2017; Zhang *et al.*, 2022) and Raman (Bai *et al.*, 2019; Zhang *et al.*, 2017) investigations.

Analysis of Parasitic Electrolyte Decomposition Reactions

During battery cycling, the generated Li_2O_2 (or LiO_2) species could potentially react with electrolyte and with the carbon cathode, giving rise the parasitic electrolyte decomposition reactions with gaseous byproducts generation like H_2 , CO_2 and NO_2 , and thus the ubiquitous capacity fading and eventually cell failure. (Freunberger *et al.*, 2011; Xu *et al.*, 2011a; McCloskey *et al.*, 2012c) *In situ* DEMS, together with the aforementioned FT-IR spectroscopy, has been widely deployed for the real time quantitation of those gaseous by-products, providing comprehensive information on revealing the electrolyte decomposition mechanism.

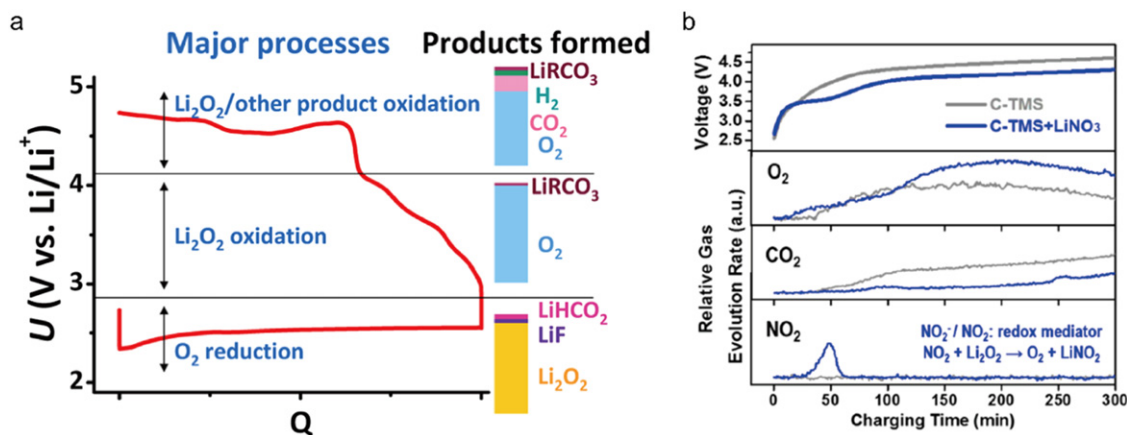


Fig. 9 Representative DEMS studies on electrolyte decomposition and electrochemical reversibility in LOBs. (a) Schematic illustration of major products distribution during charge/discharge processes. (b) Comparison of O₂ reversibility and side products distribution upon the adding of NO₃[−] into concentrated sulfolane electrolyte. Reprinted with permission from McCloskey, B.D., Valery, A., Luntz, A.C., *et al.*, 2013. Combining accurate O₂ and Li₂O₂ assays to separate discharge and charge stability limitations in nonaqueous Li-O₂ batteries. *J. Phys. Chem. Lett.* 4, 2989–2993. Copyright 2013 American Chemical Society. Li, Z., Song, C., Dai, P., *et al.*, 2022c. Nonvolatile and nonflammable sulfolane-based electrolyte achieving effective and safe operation of the Li-O₂ battery in open O₂ environment. *Nano Lett.* 22, 815–821. Copyright 2022 American Chemical Society.

McCloskey and co-workers (McCloskey *et al.*, 2011, 2012a, 2013), have combined DEMS analysis with other quantitative techniques to systematically investigate the instability issues in LOBs, suggesting that Li₂O₂-induced electrolyte solvent and salt instabilities account for nearly all efficiency losses upon discharge, whereas both cathode and electrolyte instabilities are observed upon charge at high potentials. As schematically shown in Fig. 9(a), Li₂O₂ is primarily oxidized to evolve O₂ in DME-based cells at low potentials. However, Li₂O₂-induced electrolyte and carbon cathode oxidation occurs to form interfacial carbonate layers, while electrolyte decomposition products formed during discharge are also oxidized. The carbonate at the Li₂O₂-electrolyte interface drives the cell potential above 4 V, at which point electrolyte and cathode decomposition accelerates, leading to both CO₂ and H₂ evolution from decomposition products toward the end of charge. Li *et al.* (2022c) described a LOB invulnerable for open O₂ environment operation by using a concentrated sulfolane (C-TMS) solvent. As shown in Fig. 9(b), with the introduction of LiNO₃ into C-TMS electrolyte, the electrochemical reversibility of Li₂O₂/O₂ conversion and the compatibility between Li metal anode and electrolyte have been improved, *i.e.*, more O₂ generated but less CO₂ byproduct during charge. They proposed that NO₃[−] dissolved in TMS electrolyte can act as a redox mediator, which was reinforced by the evolution of trace NO₂ in initial stage of first charging process.

Isotope Labeling

Based on its working principle of assessing specific *m/z* concentration, DEMS exhibits a unique advantage with isotope labeling to tackle two fundamental questions in LOBs, *i.e.*, what's the chemical nature of reactive key intermediates, and where do the battery reactions take place? (Yan *et al.*, 2021).

As a representative response to the first question, Luntz *et al.* (McCloskey *et al.*, 2011) coupled quantitative DEMS investigation with isotopic ¹⁸O₂ labeling to study the Li-O₂ electrochemistry in carbonates and dimethoxyethane (DME) solvents. They found that employing pure DME as solvent results in predominantly Li₂O₂ formation during discharge. In addition, O₂ is mainly produced during cell charging, although at a rate lower than expected from the amount of O₂ consumed during discharge. Isotopic ¹⁸O₂ labeling confirms that the O₂ evolved during cell charge was that consumed from the cell headspace during discharge (Fig. 10(a)). CO₂ is only produced near the end of charge and is coincident with an increase in the cell potential from 4.5 to 4.6 V. On the other hand, in the carbonate-containing solvents, the dominant discharge chemistry could be described as carbonate decomposition. Li alkyl-carbonates and a small amount of Li₂O₂ were observed in the cathode after discharge. As a result, CO₂ is the dominant species evolved at high potentials of 4.5–4.6 V during charging of these cells.

As discussed in Section “Analysis of Reaction Interfaces” of Raman studies on the reactive interface assessment, DEMS coupled with isotope labeling actually provides a different insight. Lu *et al.* (Wang and Lu, 2019) studied the reaction interface in a regular Li-O₂ cell operating conditions using time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and *in situ* DEMS with isotope labeling (Fig. 10(b)). By discharging the LOBs in ¹⁶O₂ gas followed by ¹⁸O₂, a core@shell structured Li₂O₂ particle has been constructed by TOF-SIMS, consisting of a Li₂¹⁸O₂-enriched outer shell exposing to the electrolyte and a Li₂¹⁶O₂-enriched inner core contacting the electrode. This Li₂¹⁶O₂@Li₂¹⁸O₂ configuration therefore indicates that the ORR active sites locate at the Li₂O₂/electrolyte interface. Moreover, upon charging, ¹⁸O₂ signal was firstly released as captured by time-resolved DEMS, followed by ¹⁶O₂ species, which demonstrated that OER took place at the Li₂O₂/electrolyte interface. Similar assignments of ORR/OER reactive interface at the presence of redox mediators have been proposed by Nishioka *et al.* (2021) using a similar DEMS approach. Noteworthy, these conclusions are contrast to previous Raman results shown in Fig. 3(c). In a recent review, Lu *et al.* proposed that

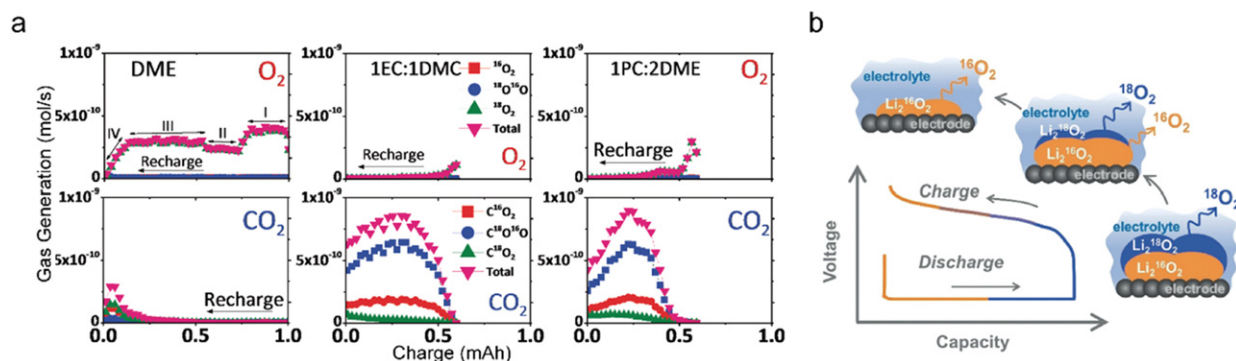


Fig. 10 Isotope labeling design in Li-O₂ battery detected by DEMS. (a) isotopically labeled O₂ and CO₂ gas evolution during charging of DME-based, 1:1 (v:v) EC/DMC-based, and 1:2 (v:v) PC/DME based cells. (b) schematic illustration of Li₂O₂ oxidation process during charging. Reprinted with permission from McCloskey, B.D., Bethune, D.S., Shelby, R.M., Girishkumar, G., Luntz, A.C., 2011. Solvents' critical role in nonaqueous lithium-oxygen battery electrochemistry. *J. Phys. Chem. Lett.* 2, 1161–1166. Copyright 2011 American Chemical Society. Wang, Y., Lu, Y.C., 2019. Isotopic labeling reveals active reaction interfaces for electrochemical oxidation of lithium peroxide. *Angew. Chem. Int. Ed.* 58, 6962–6966. Copyright 2019 Wiley-VCH Verlag GmbH & Co.

the major source of discrepancy responsible for these opposite conclusions lies in the operating condition, *i.e.*, the applied current density/voltage, the type of electrolyte used and the morphology/crystallinity/surface chemistry of the Li₂O₂ which are determined by how Li₂O₂ particles are formed/loaded in the experiments (Wang and Lu, 2020).

Closing Remarks

In summary, the implementation of advanced *in situ* spectroelectrochemical techniques within nonaqueous Li-O₂ batteries leads to a deepened mechanism understanding on their charge/discharge reactions, shedding light on the optimization strategies to further improve the energy capabilities of LOBs. For an ideal LOB, it involves a reversible Li₂O₂-mediated ORR/OER cycle at cathode surface, enabling the roundtrip efficiency and the cycle life of cells. *In situ* electrochemical SERS and FT-IR provide complementary information on the superoxide and/or peroxide chemistry at molecular level. Specifically, the growth mechanism of Li₂O₂ during ORR has been revealed to follow *via* either a solution pathway or a surface pathway, in which the former is recognized to substantially increase the cell discharge capacity. In practical LOB operations, a large charging overpotential is usually noted as due to the formation of insulating Li₂O₂ at cathode as well as the inevitable parasitic side-reactions of electrolyte and/or cathode oxidation under active oxygenated species attacking. *In situ* FT-IR has been deployed to evaluate the electrolyte stability, and DEMS has been deployed to assess the Coulombic efficiency and the O₂ recovery efficiency, in together guiding the development of more robust cell components design.

Noteworthy, regardless of the reversible ORR/OER processes or the side reactions in LOBs, solid assignments of the key reactive intermediates and the reactive interface during battery cycling are yet contentious, relying on the development of more advanced characterization methods at even higher temporal-spatial resolution, and the comprehensive validation from spectroelectrochemistry, isotope labeling and theoretical simulations. For instance, *in situ* electron paramagnetic resonance spectroscopy could aid to clarify the dynamic evolution of superoxide radical species evolution in electrolyte, and the coupling of ATR-IR-DEMS could detect simultaneously both the surface adsorbed intermediates and the volatile species evolution information for a better understanding of Li-O₂ chemistry and the further advancement of Li-O₂ technology.

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Batteries, Rechargeable

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Abstract

A battery is a device that converts the chemical energy contained in its active materials directly into electrical energy by means of an electrochemical oxidation–reduction reaction. Rechargeable batteries are secondary storage cell which can be charged and discharged into a load many times as opposed to primary storage cell which should be disposed after one time usage. Rechargeable batteries find application in devices including portable consumer device, light vehicles, automobile starters, uninterruptible power supply etc. This article presents a detailed discussion of rechargeable batteries including Nickel-Cadmium, Nickel-Metal Hydride and Lithium-Ion. The charging and discharging mechanism, active materials that is used as anode and cathode, separators and its reaction of the three batteries are elaborated. Also, the performance, capacity, challenges and applications of the three batteries are discussed.

Key Points

- Charge/Discharge mechanism of rechargeable Batteries such as Ni-Cd, Ni-MH and Li-Ion.
- Nickel hydroxide electrode as cathode active material and Cadmium as anode active materials for Ni-Cd battery and its reactions.
- Environment impact of Ni-Cd battery working.
- AB₅-Type Metal Hydride Electrodes as anode active materials for Ni-MH battery and its reactions.
- Carbon as anode active material and Lithiated Oxides as cathode active materials for Li-Ion battery and its reactions.
- Comparison, challenges, opportunities and application of Ni-Cd, Ni-MH and Li-Ion batteries.

Introduction

As electrical and electronic devices become increasingly essential parts of modern society, we are ever more dependent on our sources of electrical power. Batteries are one of the few practical methods of storing electrical energy. As such, they are vital components in electrical and electronic devices ranging from cellular phones to satellites in space. Recent advances in battery technology, both in new battery types and in improvements to existing batteries, have fueled a surge in battery applications. As battery applications become more diverse and more critical to system operation, it is especially important that system designers and users understand the fundamentals of battery function.

Batteries can be roughly divided into primary and secondary batteries. Primary batteries, such as the very popular alkaline–manganese batteries, cannot be electrically charged. However, secondary batteries (rechargeable batteries) can be electrically charged, which offers savings in costs and resources. The market demand obviously is a strong driving force for the research and development of rechargeable batteries.

The rapid development of and demand for portable cordless consumer electronics such as video cameras, shavers, power tools, cellular phones, laptop computers, and, in particular, electric vehicles (EV), and hybrid electric vehicles (HEV) demand high-performance power sources; that is, compact, high-energy, high-power, long-lasting, and maintenance-free rechargeable batteries. Nickel–cadmium (NiCd) has been a very important power source since the 1960s. Since 1980, the variety of practical batteries has increased dramatically. Recently, the market for nickel–metal hydride (NiMH) and lithium-ion batteries (Li-Ion) has been developed and has grown remarkably.

A battery is a device that converts the chemical energy contained in its active materials directly into electrical energy by means of an electrochemical oxidation–reduction (redox) reaction. ‘Battery,’ which is a term often used in practical application and manufacturing, is an assembly of one or more cells connected in series or parallel (or a combination), depending on the requirements of the output voltage and capacity. ‘Cell’ is the basic electrochemical unit consisting of major components and undergoing essential chemical reactions to generate electrical energy for use. At least two reaction partners undergo a chemical process during reaction. The energy of this reaction is available as electric current at a defined voltage and time. A characteristic feature of an electrochemical cell is that the electrochemical processes at the electrodes generate the electronic current, which is the movement of electrons in the external circuit. In contrast to the electronic current, the charge is transported between the positive and the negative electrode in the electrolyte by ions.

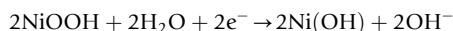
In this section, the fundamental aspects, properties, performance, and applications of rechargeable batteries, including NiCd, NiMH, and Li-Ion systems will be discussed. In this article, the terms ‘battery’ and ‘cell’ are generally used interchangeably.

Nickel–Cadmium Batteries

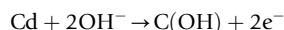
The NiCd cell has a unique set of desirable physical and electrical characteristics. Although NiCd cells can be designed and manufactured in different forms and a variety of sizes, the basic chemistry remains the same. The NiCd cell is an electrochemical system in which the active materials contained in the electrodes change in oxidation state without any deterioration in physical state. These active materials are present as solids that are insoluble in the alkaline electrolyte. Unlike many other systems, in the NiCd system, its charge and discharge reactions do not require the transfer of material from one electrode to the other. The electrodes are long lasting, since the active materials in them are not consumed during operation or storage.

Charge/Discharge Reactions

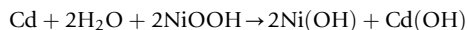
In the NiCd cell, nickel oxyhydroxide, NiOOH , is the active material in the charged positive electrode. During discharge it is reduced to the lower valence state, nickel hydroxide, Ni(OH)_2 , by accepting electrons from the external circuit:



Cadmium metal is the active material in the charged negative electrode. During discharge, the cadmium is oxidized to cadmium hydroxide, Cd(OH)_2 , and releases electrons to the external circuit:



The net reaction occurring in the potassium hydroxide (KOH) electrolyte during discharging can be expressed as follows:



while during charging, these reactions reverse directions.

Sealed cells are today the dominant form of NiCd battery, which can provide convenient, clean, reliable, and maintenance-free services. Sealed NiCd cells are usually made in cylindrical shapes. It uses a wound plate, sealed construction with a nickel-plated steel can as the negative terminal, and a metallic cover as the positive terminal. The cell cover is an assembly that includes a high-pressure safety vent mechanism and insulating ring. Each electrode, which is a continuous conductive strip containing active material, is isolated from the other electrode by a separator; a nonconducting, porous, fibrous, and polymeric material. The two electrodes and their accompanying separators are wound together into a roll configuration. This roll is then inserted into a can. **Fig. 1** shows a cutaway of a typical sealed cell (Gates Energy Products, 1989). In **Fig. 2**, discharge curves of a sealed NiCd cell at different rates at room temperature are displayed. It can be seen that the cell is capable of delivering energy at very rapid rates.

Recombination Reactions in the Sealed Operation

The sealed cells normally operate at internal pressures well below the vent pressure because the gas evolved during charging is readily recombined. To accomplish this feature, the capacity of the negative electrode must be greater than that of the positive one (the so-called positive limited design). As a result, the positive electrode achieves full charge and emits oxygen before the negative electrode is fully charged and emits hydrogen, which cannot be readily recombined. The electrolyte solution (KOH) must be uniformly distributed by the separator, as a thin film across the surface of the two electrodes. Oxygen gas must be free to pass

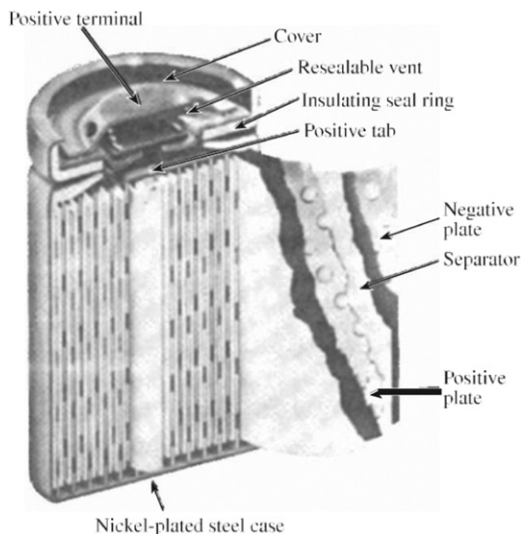


Fig. 1 Cutaway of a typical cylindrical NiCd cell. Courtesy of Gates Energy Products, 1989. Sealed Rechargeable Batteries: Application Manual. Oxford: Butterworth-Heinemann.

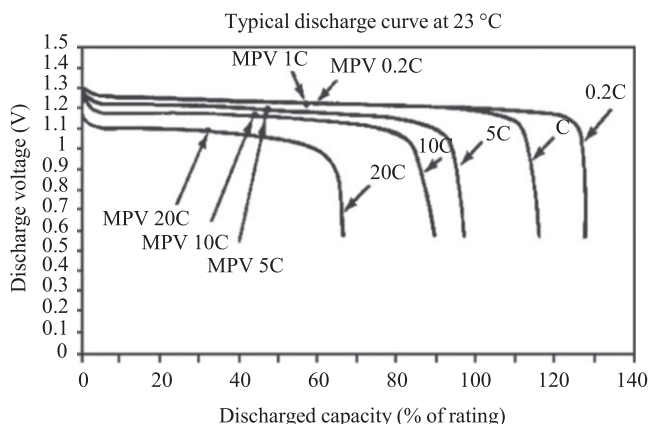
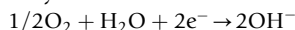


Fig. 2 Discharge curves of a sealed NiCd cell at different rates at room temperature.

between the electrodes. There must be sufficient open area in and around the electrolyte and separator for oxygen to diffuse efficiently from the positive electrode to the negative electrode.

In charging a sealed NiCd cell, the positive electrode will reach full charge before the negative electrode. At this stage, additional charging causes the positive electrode potential to rise until all the incoming current is oxidizing hydroxyl ions and generating oxygen gas at the positive electrode:

The oxygen generated at the positive electrode diffuses rapidly to the negative electrode where it is reduced back to hydroxyl ions:



Thus, in overcharge, all the current generates oxygen that is subsequently recombined. The process described above is called oxygen recombination. The oxygen pressure initially increases but stabilizes at a low equilibrium pressure determined by the cell design, the ambient temperature, and the charge rate. It is important to remember that the recombination of oxygen is an exothermic reaction. When the cell is in overcharge, essentially all of the energy in the current coming in is converted to heat. With proper matching of the charger to the battery and attention to battery location and heat dissipation, the battery system can be designed to reach a thermal steady state.

Cathode Active Material – Nickel Hydroxides

Nickel hydroxides have been used as the active material in the positive electrodes of several alkaline batteries, including the NiCd system, for over a century. Because of the commercial importance of NiCd batteries and, in particular, of NiMH batteries, the nickel oxyhydroxide materials continue to attract much attention. The most significant advances in the understanding of the overall reaction of the nickel hydroxide electrodes was made by Bode and his co-workers (McBreen and Besenhard, 1999). It was established that both the discharged material ($\text{Ni}(\text{OH})_2$), and the charged material (NiOOH), could exist in two forms. One form of $\text{Ni}(\text{OH})_2$, which was designated as $b\text{-Ni}(\text{OH})_2$, is anhydrous and has a layered brucite ($\text{Mg}(\text{OH})_2$) structure as shown in Fig. 3.

The other form, $a\text{-Ni}(\text{OH})_2$, is hydrated and has intercalated water between brucite-like layers. Oxidation of $b\text{-Ni}(\text{OH})_2$ on charge produces $b\text{-NiOOH}$, and oxidation of $a\text{-Ni}(\text{OH})_2$ produces $g\text{-NiOOH}$. Discharge of $b\text{-NiOOH}$ yields $b\text{-Ni}(\text{OH})_2$ and discharge of $g\text{-NiOOH}$ yields $a\text{-Ni}(\text{OH})_2$. The two reaction schemes are often referred to as the b/b and the a/g cycles. On discharge, the $a\text{-Ni}(\text{OH})_2$ can dehydrate and recrystallize in the concentrated alkaline electrolyte to form $b\text{-Ni}(\text{OH})_2$. Also, $b\text{-Ni}(\text{OH})_2$ can be converted to $g\text{-NiOOH}$ when the electrode is overcharged. Their overall reaction scheme is shown schematically in Fig. 4. It is also found that the transformation of $b\text{-Ni}(\text{OH})_2$ to $b\text{-NiOOH}$ experiences some degree of volume expansion, while when the $b\text{-Ni}(\text{OH})_2$ converts to $g\text{-NiOOH}$, its volume increases drastically.

Therefore, conventional nickel hydroxide electrodes are designed to operate on the b/b cycle in order to accommodate the volume change that occurs during cycling, since the b/b cycle results in less volume increase. During the b/b transformation, the theoretical capacity of the $b\text{-Ni}(\text{OH})_2$ is 289 mAh g^{-1} . The discharged phase of the positive electrode, $b\text{-Ni}(\text{OH})_2$, is a poor electrical conductor. The conductivity of $b\text{-NiOOH}$ is more than five orders of magnitude higher than that of $b\text{-Ni}(\text{OH})_2$. As a result, there is difficulty in the charge/discharge processes, particularly the discharge, because the resistive discharged products cause the electrode not to be discharged at a useful rate. Operation on the b/b cycle is ensured by the use of a combination of additives such as cobalt, cobalt oxide, and zinc, as well as by the control of the electrolyte composition.

In the NiCd cell, the nickel hydroxide electrodes can be made using either sintered or foam substrate materials into which the active material is deposited. In the case of sintered electrodes, a layer of high-surface-area and dendritic-type nickel powder is coated on a steel foil strip (up to 100 mm thick). The coated strip is passed through a high-temperature furnace having a reducing atmosphere, and the dendritic projections of the nickel powder fuse together forming a strong, highly porous substrate material known as nickel plaque. Nickel

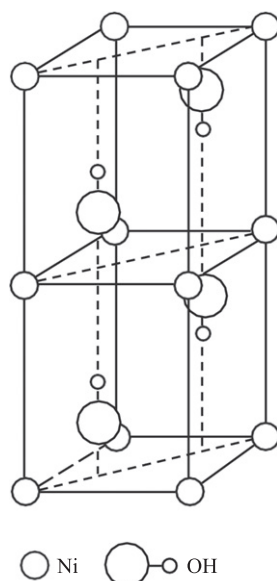


Fig. 3 The brucite structure of $\text{Ni}(\text{OH})_2$ showing the orientation of the O–H bonds (after McBreen, J., Besenhard, J.O., 1999. Handbook of Battery Materials. New York: Wiley-VCH).

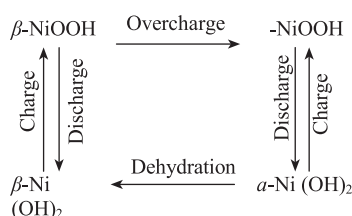


Fig. 4 Reaction scheme of nickel hydroxide electrodes.

hydroxide, the active material, is impregnated into the pores of the nickel plaque either by a chemical impregnation process or by an electrochemical technique. The sintered electrodes offer excellent high-rate discharge capabilities.

For the foam electrode, the paste of powdered nickel hydroxide along with other additives is mechanically pasted, compressed, or sprayed into the pores of the foam substrate. The larger amount of active material, which is accommodated by the larger pores and higher pore volume of the foam, results in positive plates whose energy density is 15%–20% higher than that of sintered electrodes. However, the large open structure of the nickel foam substrate may cause variations of charge distribution. To improve charge-distribution variations resulting from the foam's open structure, conductive additives such as cobalt, cobalt oxide, and/or cobalt hydroxide are mixed with the active $\text{Ni}(\text{OH})_2$ material.

A spherical, high-capacity $\text{Ni}(\text{OH})_2$ powder (Ohta *et al.*, 1994) has been developed to increase the energy density of the foam-type positive electrodes. In addition, additives such as cobalt, zinc, and/or cadmium by coprecipitation can reduce the electrode swelling which results from phase transformation during charge and discharge cycling. Nickel electrode swelling is believed to be the primary cause of electrode failure. High-performance nickel foam with fine structure and high porosity has become the norm. Thin, chemically stable separators are being developed to reduce interelectrode spacing. In turn, the volume in the cell available for active materials is increased.

Anode Active Materials – Cadmium

The theoretical capacity of cadmium metal is 480 mAh g^{-1} . However, cadmium is not usually applied as a metal to form a battery anode. The cadmium electrode may be formed starting with a mixed cadmium hydroxide, and/or cadmium oxide and a certain amount of cadmium powder. Two types of cadmium electrode are also widely used. One is the pasted cadmium electrode. Pressing the paste of mixed cadmium with a binder and additives on a nickel-plated steel foil substrate makes the pasted electrode. Due to high hydrogen over-voltage of cadmium in the caustic electrolyte, no amalgamation is needed. Another type of cadmium electrode is the sintered one, incorporating the paste of mixed cadmium material with binder and other additives in the pore system of a sintered nickel plate, which then undergoes a sintering process. The sintered cadmium electrodes provide the capability of high discharge rates when compared to pasted electrodes.

Separators

Separators generally serve two primary functions: (1) keeping the positive electrode physically apart from the negative in order to prevent any electronic current passing between them, and (2) permitting an ionic current with the least possible hindrance. To meet the two opposing requirements, the separator materials must be thin, porous, mechanically durable, chemically stable, and electrically resistant.

Two kinds of fabric materials are widely used as separators for NiCd batteries: polyamide ('nylon') and polyolefin, which can be polypropylene (PP), or polyethylene (PE), or a combination. In the case of sealed batteries, these fabric materials have proven themselves. As discussed above, the working principle of the sealed batteries is based on internal oxygen consumption. During the charging step, the positive electrodes reach their fully charged state earlier and start to evolve oxygen, which migrates through voids in the electrolyte to the negative electrode to discharge cadmium and form water. Therefore, the separator has to be permeable to gaseous oxygen. This is achieved by the separator pores being of a specific minimum size and not all of them being filled with electrolyte, thus leaving some gas channels. Due to their pore-size distribution, these fabric materials can simultaneously absorb sufficient electrolyte and allow oxygen transfer.

For longer cycle life and better charge retention, in particular for higher-temperature application (up to 60°C), polypropylene fleeces are preferred since they offer better chemical stability and do not contribute to electrolyte carbonation. However, polypropylene has to be pretreated by fluorination, or by coating and crosslinking with hydrophilic substances (e.g., polyacrylic acid) on the surface of the fiber to improve electrolyte absorption.

Cylindrical cells are manufactured automatically at very high speed, in which a layer of separator material is spirally wound, each with two electrodes. High energy density requires the separator to be very thin (0.05–0.3 mm). All these make the separator mechanical strength an important criterion. The melt-blown polypropylene fleeces (Bohnstedt and Besenhard, 1999) can be made with very thin fiber and provide low-cost hydrophilization, giving attractive properties such as small pore size, and excellent tensile performance for use in highly automated assembly processes. In this aspect, the production of melt-blown polypropylene fleeces with their excellent tensile properties offers an interesting option.

A high density and high-performance positive electrode active material for alkaline nickel based rechargeable batteries with Al-substituted α -Ni(OH)₂ powder sample is synthesized using polyacrylamide (PAM) assisted two step drying method. The drying is followed by hydrothermal treatment at 140°C for 2 h. The hydrothermal treatment improves the crystallinity of α -Ni(OH)₂ and promote the anion exchange of NO₃[−] by OH[−] resulting in good electrochemical performance. The tap-density of the resulting powder reaches 1.84 g cm^{−3}, which is significantly higher than that of α -Ni(OH)₂ powders obtained by the conventional co-precipitation (CCP) and hydrothermal (HT) methods. Compared with commercial spherical β -Ni(OH)₂, the resulting sample is electrochemically more active, providing discharge capacities of 315.0 and 255.2 mAh g^{−1}, and volume capacities of 579.6 and 469.6 mAh cm^{−3} at rates of 0.2 and 5°C, respectively. The sample synthesized by this method has outstanding performance at lower cost (Jing et al., 2014a,b). The electrochemical performance of high-density Al-substituted α -Ni(OH)₂ with interlayer NO₃[−] can further be improved by simple anion exchange method at room temperature using NaCl solution. The resulting Cl[−] intercalated α -Ni(OH)₂ sample has the high tap density, same as hydrothermal method, with enhanced activation rate. Also, it shows very high rate of discharge and excellent cycle stability. The method is simple and conducive to mass production. The cyclic voltammetry and electrochemical impedance spectroscopy show that these performance improvements are ascribed to the higher proton diffusion coefficient and the lower charge transfer resistance (Jing et al., 2015).

Applications

As one of the most popular alkaline secondary batteries, NiCd is available in several cell designs and in a wide range of sizes. Cells with different design and internal construction are provided for the needs of various applications in different environment conditions. The vented pocket-type cells are used in heavy-duty industrial applications, such as mining vehicles, railway signaling, materials-handling trucks, diesel engine starting, and emergency or standby power.

This type of battery is very rugged and can withstand both electrical and mechanical abuses, has very long life and requires little maintenance except an occasional topping up with water. The sintered-plate construction has higher energy density that provides high discharge rates and low temperature performance, which are used in applications requiring lighter weight and superior performance, such as aircraft starting, communication, and electronics equipment. The clean, maintenance-free sealed cells are available in prismatic, button, and cylindrical configurations and are used in consumer applications such as wireless phones, cellular phones, lighting, shavers, radios, etc., and small industrial applications. The high-rate discharge capability makes them ideal batteries for use in devices such as power tools and appliances, which demand high power. The sealed NiCd battery is one of many candidates for electrical-vehicle applications.

The advantages of NiCd batteries are the flat discharge curve, extremely good cycle life, very high discharge rate, and low cost. It is recommended to slow charge the new NiCd battery for 24 h before use. This charge will help the electrolyte to get redistributed and overcome dry spots on the separator. Such dry spots may appear when the electrolyte gravitates to the bottom of the cell during long storage. A slow charge also helps to bring all the individual cells back up to an equal charge level because each cell may have self-discharged to different capacity levels during storage. On the other hand, the electrochemical equivalent (480 Ah g^{−1}) is one of the lowest for all metallic anodes and the open circuit voltage of 1.35 V for the NiCd cell is not favorable for many applications. Additionally, the use of cadmium should be restricted for environmental reasons. One of the main advantages of

NiMH batteries over NiCd batteries is the environmental aspect. The replacement of NiCd by NiMH, which offers better performance and is more environment-friendly, is a strong trend.

Impact of working of NiCd Batteries

When the Ni-Cd batteries used in pocket electrodes operate for long-term, excess of hydrogen gets accumulated at the electrodes. The amount of hydrogen stored were experimentally studied by [Nikolay et al. \(2021\)](#). For this experimental study, nickel-cadmium batteries produced by different manufacturers from KL-125, KL-80, KL-28, KL-14, SBLE 110, SBM 112 and SBH 118 of different capacities were used. In the first five years of operation of Ni-Cd batteries, the accumulation of hydrogen at the electrodes increases and it reaches maximum capacity. After five years of operation, the hydrogen volume storage stops increasing. The results of the experiment showed that the total energy density of the hydrogen stored in the active substance of the oxide-nickel electrode was equal to 79.40 kJ g^{-1} and $160.24 \text{ kJ cm}^{-3}$. Also, it was observed that the specific storage capacities of the hydrogen in the active substances of the electrodes of these batteries are the same, regardless of the batteries' capacities and manufacturers.

Ni-Cd battery manufacturing and its operation leads to environmental impact that cause the evolution of certain gases that are toxic to the environment and produce harmful effects. A life cycle assessment of Ni-Cd battery was conducted by [Nitin Kotkunde et al., 2021](#), in which the energy input required by the Ni-Cd batteries was identified and the environmental impact produced by them are detailed. The energy required for processing, manufacturing, usage and transportation during the lifecycle of Ni-Cd batteries and the environmental impact such as toxic gases evolved, solid and liquid wastes produced during the lifecycle of Ni-Cd batteries was addressed. The assessment was conducted by collecting real time industrial data. Accordingly, the total energy input required for the development of nickel cadmium battery is 1,637,802 (Wh). Due to heavy metal extraction and emission during different development stages, the global warming potential, human toxicity, photochemical Oxidants creation, Eutrophication potential and acidification potential exhibits impacts that dominates the impact of usage of Ni-cd batteries in long-term applications.

Nickel–Metal Hydride Batteries

The NiMH battery is a viable alternative to NiCd, which has been widely used in portable electronics since the 1960s. The 30%–50% higher energy density, nontoxic, and environmentally friendly constituents, as well as plentiful raw materials, make the NiMH superior to the NiCd battery. Since 1980, extensive application-oriented research and development work has been conducted on metal hydride (MH) alloys, MH electrodes, and NiMH batteries. NiMH rechargeable batteries have become increasingly popular.

since they were commercialized in 1990. This is the most successful application of hydrogen absorption materials and hydride technology. Research and development work on the MH materials and NiMH battery has been extensively reviewed ([Sakai, 1995](#); [Notten, 1995](#); [Zhang, 1997](#)).

Charge and Discharge Reactions

The high-energy-density NiMH cell is a combination of NiCd technology and the advanced metal hydride materials. In other words, when MH alloys are used to replace cadmium as the active material in the negative electrode, a NiCd cell becomes a NiMH cell. The concept of a NiMH cell consisting of nickel electrode (+) and AB_5 metal-hydride electrode (–) is schematically represented in [Fig. 5](#). The electrodes are insulated electrically from each other by a separator that is usually fibers made from either polyamide or polyolefin in the form of nonwoven fabrics. An alkaline solution, KOH, is the electrolyte, which provides ionic conductivity between the two electrodes. During charging, at the positive electrode the nickel hydroxide, $\text{Ni}(\text{OH})_2$, is oxidized to nickel oxyhydroxide, NiOOH . All of these are the same as in the NiCd cell discussed in the previous article.

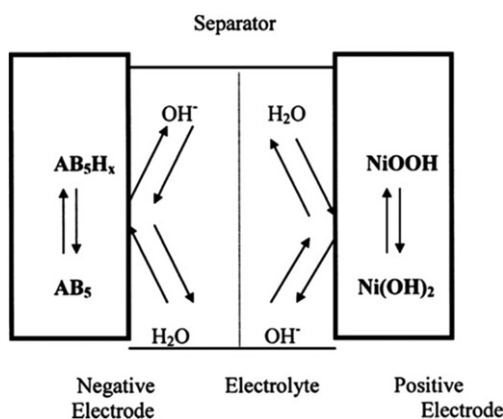


Fig. 5 Schematic representation of charge (↑) and discharge (↓) reactions of a rechargeable NiMH cell.

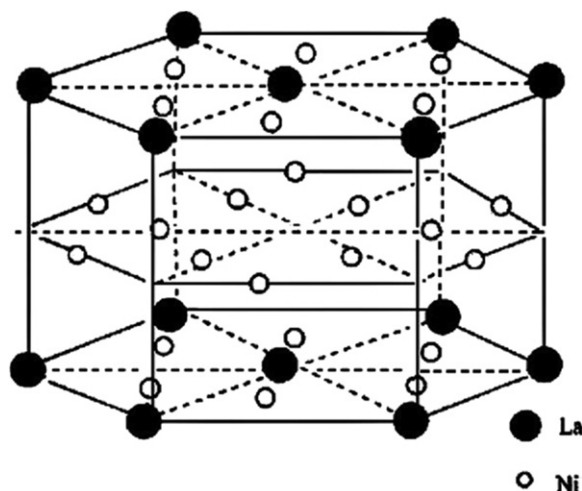
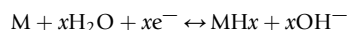


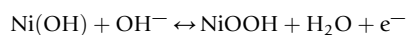
Fig. 6 Schematic of hexagonal lattice of LaNi_5 intermetallic compound.

However, at the negative electrode, the metal hydride alloy forms hydride by absorbing hydrogen which is generated from water electrolysis. The electrochemical reactions during the charge and discharge cycle can be expressed using the following equations:

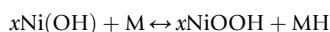
MH electrode (−):



Ni electrode (+):



Overall reaction:



A key consideration underlying the development of a sealed NiMH cell is to prevent the buildup of hazardous gas pressure, due to oxygen and hydrogen evolution which results in the loss of electrolyte. This is achieved by balancing the quantity of active materials of the positive and the negative electrodes. In the NiMH cell, the MH electrode is designed to have higher capacity than the $\text{Ni}(\text{OH})_2$ counter. The excess MH materials are called ‘charge reserve.’ Ideally, the negative electrode should never be fully charged. However, a small amount of overcharge is necessary to ensure that the cell is fully charged. In principle, hydrogen gas is generated as the negative electrode is absorbed by hydride alloy via gas-phase reaction, while the oxygen generated at the positive electrode penetrates through the separator and diffuses to the MH electrode. The oxygen is reduced at the MH/electrolyte interface to form hydroxyl ions. This complicated and multistep process is called oxygen recombination, which is similar to that in NiCd batteries discussed in the previous article.

The charge/discharge performance of NiMH batteries at elevated temperatures above 70°C , can be improved by introducing additive materials in the electrolyte. This process imparts superior electrode properties with enhanced discharge capacity, very high discharge rate and excellent stability at high temperatures. Also, the electrodes containing additives has performance improvement due to the increased oxygen evolution over potential, slower oxygen evolution rate and lower electrochemical impedance. [Jing et al. \(2014a,b\)](#), proposed uniform dispersal of 0.5 wt% calcium metaborate (CMB) in the nickel electrode to attain superior electrode properties and performance improvement at high temperatures. However, electrochemical impedance spectroscopy (EIS) studies show that the CMB have little effect on electron transfer resistance of nickel electrode. [Shangguan et al. \(2013\)](#) proposed sodium metaborate (NaBO_2) additive for NaOH electrolyte that exhibits improved electrode properties with very good charge retention. The charge acceptance of these NiMH batteries at elevated temperatures is over 96% at charge/discharge rate of 1 C. EIS studies show that the charge transfer resistance is reduced. In a further study ([Shangguan et al., 2014](#)), it was found that 1.0 wt% of sodium tungstate (Na_2WO_4) as additive in two types of electrolytes (KOH and NaOH) shows significant improvement in nickel electrode performance for both electrolyte at elevated temperatures. Coating solid film $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ on the surface of nickel electrode also shows performance improvement.

Anode: AB_5 -Type Metal Hydride Electrodes

There are many intermetallic compounds that exhibit the ability to reversibly absorb large amounts of hydrogen, among which a number of MH alloys have been evaluated for battery applications ([van Rijswijk, 1978](#)), such as the LaNi_5 , $\text{La}_{0.8}\text{Nd}_{0.2}\text{-Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$, $\text{Mm}(\text{NiCoMnAl})_5$ system, the TiNi, Ti_2Ni , $\text{TiMn}_{0.5}$, Ti–Zr-based system, and the Zr–Mn–Ni-based system. The research work on MH materials has concentrated mainly on rare earth-based AB_5 systems, which are derived from the LaNi_5 intermetallic and are considered the best materials for NiMH cells. Another system that has been extensively studied is traditionally called AB_2 , which actually includes Ti–Zr–Ni-based multiphase alloys and the Zr–Mn–Ni-based AB_2 -type Laves phase alloys.

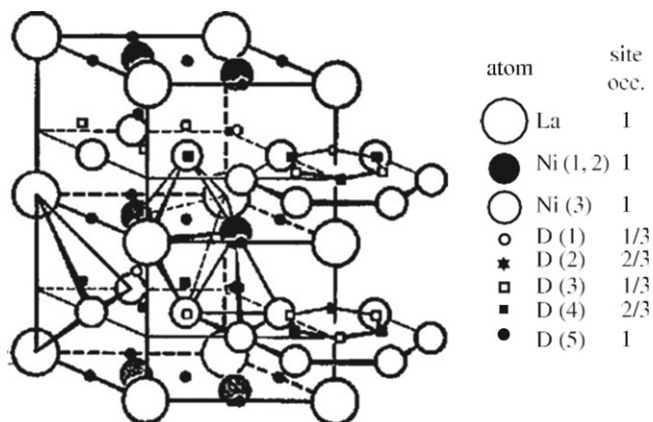


Fig. 7 Crystal structure of LaNi_5D_7 .

LaNi_5 is the starting compound for the AB_5 -type alloys, which has the hexagonal CaCu_5 structure, space group $P6/mmm$, as shown in Fig. 6. It can easily form hydride, LaNi_5H_7 , with a theoretical capacity of 372 mAh g^{-1} or 2600 mAh cm^{-3} . The crystal structure of the hydride can be illustrated, as shown in Fig. 7, by LaNi_5D_7 . However, for LaNi_5H_7 , its equilibrium pressure is higher than one atmosphere at room temperature ($P_{\text{abs}} \approx 2.3 \text{ atm}$, $P_{\text{des}} \approx 1.6 \text{ atm}$ at 25°C), making it difficult to charge.

In addition, its capacity was found to decline drastically, following an exponential pattern, during repeated electrochemical charging and discharging, which was ascribed to the decomposition of LaNi_5 caused by the corrosive action of the electrolyte. Since the 1970s, approaches have been applied to modify LaNi_5 for electrochemical use.

The charge and discharge processes of a typical commercialized AB_5 -type MH electrode in KOH are illustrated in Fig. 8. The curves are the electrochemical equivalent of the PCIs (pressure-composition isotherms) of gas phase reaction, while a graphic description of phase transformation is displayed. Actually, there is a thermodynamic correlation between the equilibrium pressure measured in the gas phase reaction and the electrode potential measured in an electrochemical cell (Notten, 1995):

$$E/\text{V} - 0.932 - 0.029 \log P_{\text{H}_2}$$

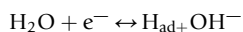
where E is in volts, and P_{H_2} is in atm. Usually, the MH alloy must be activated prior to testing.

Therefore, the starting alloy would be an α -phase which is a solid solution of hydrogen. Charging a MH electrode consists of electrolysis of water on the MH surface, generating hydrogen atoms and hydroxyl ions. This step is the charge transfer process. The generated hydrogen atoms are adsorbed on the MH surface. Ideally, the adsorbed hydrogen subsequently dissolves in the alloy to form a metal hydride β -phase, therefore a growing product layer of the β - AB_5H_x advances inward from the surface. On discharging, hydrogen atoms transport to the MH surface to react with hydroxyl ions forming water, and the hydride decomposes to α -phase alloy. Again, a growing α -phase layer proceeds inward from the surface. It should be noted that there is a competitive reaction in the charging process, in parallel with hydrogen diffusion: if the diffusion rate is slower than the charge transfer rate, the atomic hydrogen may combine to form molecular hydrogen resulting in the build-up of the internal gas pressure.

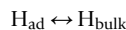
Another characteristic of the hydride alloy is that the particles will be broken down during cycling due to repeated lattice expansion/shrinkage, and ultimately to $\text{B}_3 \text{ mm}$ in diameter, along with which, a part of the active material is corroded and the cell.

internal impedance increases. The charge and discharge mechanism are described in the following equations, from which it can be seen that each absorbed or desorbed hydrogen atom corresponds to the storage or release of one electron:

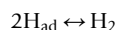
Charge transfer reaction:



Hydrogen diffusion (MH formation):



Hydrogen combination:



From the above discussion, it can be concluded that a good MH alloy for electrochemical application must meet the following properties for its optimum use in MH electrodes:

- Capacity for high energy density;
- Chemical stability for long cycle life;
- Mechanical stability to reduce the decrepitation rate;
- Rapid charge and discharge kinetics for high-rate capability;
- Rapid activation rate to allow freshly prepared electrodes to quickly respond; and
- Low cost.

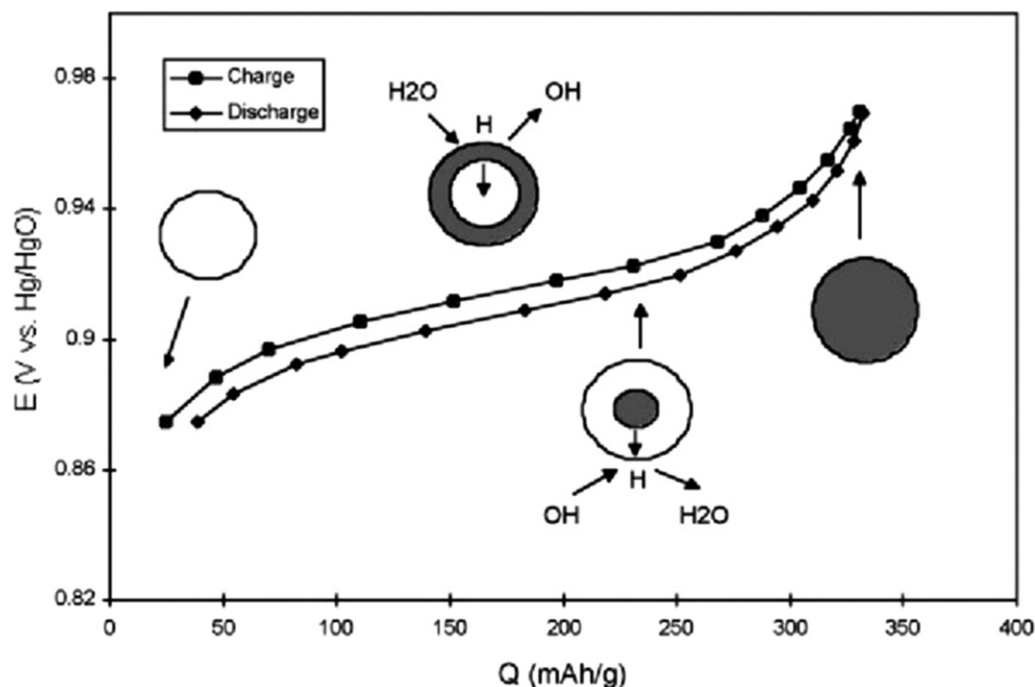


Fig. 8 Electrochemical charge and discharge processes of a typical AB_5 alloy in 8 N KOH at 25 °C. The MH alloy is subjected to phase transformation between a and b .

MH electrode characteristics strongly depend on the chemical composition of the intermetallic compounds. A considerable improvement was realized (Willems, 1984) when lanthanum was partially substituted by neodymium, and nickel by cobalt and aluminum or silicon. The substitution not only adjusted the equilibrium pressure to below 1 atm at room temperature, but also significantly improved cycle life. The cobalt substitution has the special effect of reducing the lattice expansion during charging, dramatically decreasing the lattice expansion in the c -axis direction, and in turn reducing the pulverization rate and improving cycle life. Lattice expansion along the c -axis has more influence on cracking due to the layer structure of the alloy. Furthermore, misch metal (Mm, a mixture of rare earths including lanthanum, cerium, neodymium, and praseodymium) was used to replace pure lanthanum to reduce its cost.

However, the smaller size in atomic radii of cerium, neodymium, and praseodymium compared to that of lanthanum results in the so-called 'rare earth contraction effect,' decreasing the cell volume and causing an increase in the hydrogen equilibrium pressure. Doping with manganese, in addition to cobalt and aluminum, could effectively reduce the equilibrium pressure without a decrease in capacity. The synergistic effects by alloying also showed improvement in corrosion resistance, attributed to modifications in both chemical and mechanical stability. Therefore, multicomponent AB_5 systems, with formulation Mm (NiCoMnAl)₅, were developed and considered the most suitable MH electrode.

For an AB_5 compound, its element distribution, i.e., the alloy's microstructure, plays a key role on the cell cycle life. The microstructure here involves phase distribution, grain size, grain shape, element segregation, grain boundary, etc. If the melted alloy was cooled at high rate using a plate-like casting, a clear columnar structure with a smaller grain size (20–30 nm) formed, and showed an increase in cycle life. This is explained by the columnar structure, with the c -axis in parallel to the cooling plane, having less lattice strain and less pulverization rate. In contrast, manganese facilitates nucleation, therefore the addition of more manganese resulted in an equiaxed structure and, in turn, high lattice strain. The lattice strain in the alloy facilitates the cracking and high decrepitation rate during cycling, thus the alloy displays shorter cycle life.

Melt-spinning and gas atomization can produce alloys with small grain size (10 nm), and better homogeneity. Such a fine microstructure makes the protective surface layer, for example, formed by aluminum-containing compound, to be more effective during cycling which reduces the decrepitation rate and improves cycle life. Increasing the cooling rate followed by post-heat treatment can eliminate the formation of a second phase, modify element segregation along the grain boundary and within the crystallite, remove lattice defects such as dislocations, and thus further improve cycle life. Amorphous alloys, generated either by the thin-film technique or by prolonged mechanical grinding, the $LaNi_5$ or Mm (NiCoMnAl)₅ alloys showed less decrepitation rate and longer cycle life, but also resulted in a decrease in the discharge capacity.

The alloy surface activity is an important property directly associated with electrochemical kinetics such as the rate of charge transfer reaction (water electrolysis), and the oxygen recombination reaction. Usually, the surface activity is evaluated by its exchange current density, i_0 , which can be obtained from the Tafel relationship expressed as follows:

$$Z \frac{1}{4} a - b \log i, a \frac{1}{4} 2 : 3 RT = bF \log i_0$$

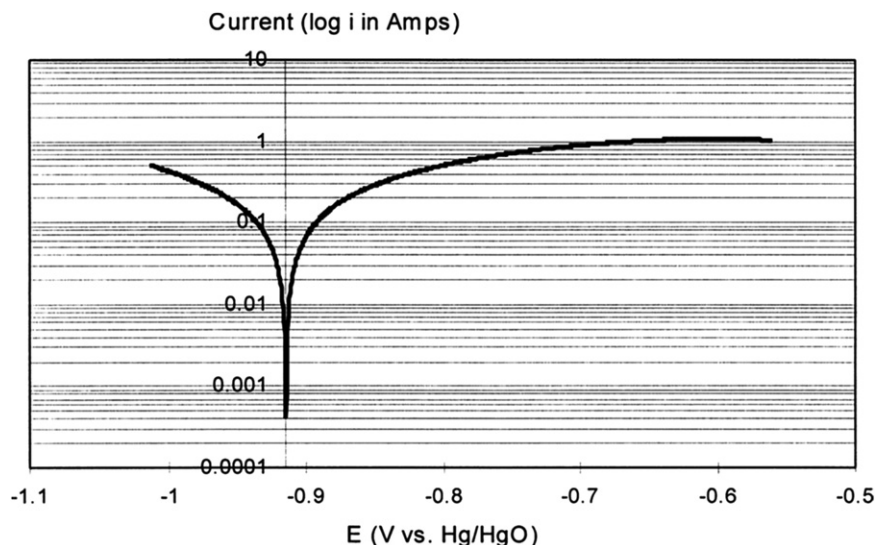


Fig. 9 Tafel plot of a typical AB_5 alloy 35% charged. The current density is expressed by amps per 250 mg MH alloy sample (0.5 mV s^{-1}).

where Z is the overpotential, i is the current density under the overpotential, Z . i_0 is the exchange current density usually expressed in A cm^{-2} . However, for MH alloys, i_0 is expressed using A g^{-1} due to its dynamic characteristics in particle-size distribution.

Fig. 9 is a Tafel plot of a representative Mm (NiCoMnAl)₅ alloy at a state of charge of 35%. On the left side of the y-axis, it is a charge process (cathodic reaction), while on the right side, a discharge process (anodic reaction). The peak point ($i \approx 0$) is the equilibrium potential, $E_{(i \approx 0)}$, of 0.92 V against Hg/HgO.

From this plot it can be seen that there is no linearity behavior between -0.91 and -0.7 V, indicating that there is no Tafel relationship in the anodic process. A similar behavior was also observed in the cathodic process. This observation suggests that for the multicomponent AB_5 system, it is not appropriate to use the Tafel equation to obtain its exchange oxides density. Instead, we can use the linear polarization technique within a small range around the equilibrium potential ($E_{(i \approx 0)}$) ($Z \approx 710 \text{ mV}$). The non-Tafel behavior is also an indication that the surface activity, and in turn the charge transfer reaction, is strongly affected by mass transport. This may involve the diffusion of hydrogen in the solid alloy, OH^- and H_2O in the electrolyte (van Rijswijk, 1978).

It is generally believed that the multicomponent AB_5 electrochemical hydrogen reaction has good kinetic properties; however, the element substitution resulted in a substantial decrease of the surface activity from that of LaNi_5 compound. The surface reactivity relies on two factors: effective reaction area, and catalytic functioning. It was reported that the rate capability of MH.

electrodes made of $\text{MmNi}_{3.6}\text{Co}_{0.7}\text{Mn}_{0.4}\text{Al}_{0.3}$ could be modified significantly by the addition of metal oxide powders, such as CuO , CoO , Y_2O_3 , and $\text{Y}(\text{OH})_3$.

Double-phase AB_5 -type alloys reported by Notten (1995) are capable of increasing the rate capability of MH electrodes. It can be considered as an alternative approach to improving the charge transfer reaction by the use of a catalyst. When additional nickel and molybdenum are put into a 'standard' alloy, $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$, the alloy will become a nonstoichiometric.

$AB_{5.5}$ material. When a highly electroactive compound MoCo_3 was generated as a second phase in the $AB_{5.5}$ alloy (e.g., $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.9}\text{Mo}_{0.1}\text{Co}_{2.4}\text{Si}_{0.1}$), the alloy's discharge efficiency was significantly improved from 190 to 600 mA g^{-1} . The enhanced surface reactivity was ascribed to the excellent catalytic activity of MoCo_3 or NiCo_3 decorating the exterior of the MH particles. The introduction of a second phase, such as MmCo_4B and MmB_4 , is also reported to improve discharge efficiency.

Fluorine treatment was initiated a few years ago. It was reported that the fluorine treatment forms a condensed LaF_3 layer on the top surface to protect the MH alloy from being corroded. The most striking progress is that nickel particles could be implanted in the RF_3 layer simultaneously during the fluorination process so as to significantly enhance the reactivity, as well as the activation and the corrosion protection, of MH materials.

Development of MH Electrode and NiMH Cells

To optimize the use of MH as active material in the NiMH cells, a great effort has been made to develop MH electrode technology. The aim of the MH electrode technology is to make MH electrodes possess an appropriate energy capacity, suitable geometric dimensions, good mechanical integrity, satisfactory electrochemical functioning, and long cycle life. At present, two different techniques for preparing MH electrodes have been developed and are widely used in the battery industry: (1) the sintering method (Fetcenko *et al.*, 1990) for Ti-Zr-V-based alloy by pressing the powder materials without additive on a nickel-mesh sheet, followed by a sintering process; and (2) the pasting method (Kinoshita *et al.*, 1996) by extruding the substrate through a slurry containing MH powder, conductive powders such as carbon, nickel, cobalt, etc., and other additives to improve the electrode conductivity and surface reactivity. The pasting technology is more complicated because the properties of the numerous additives have to be

Table 1 Examples to show the progress of a NiMH cell

Size	1991	1998
AA	1000	1000–1500
4/3 A	2500	3000–4000

optimized to obtain the desired electrode properties. The binder materials, such as polytetrafluoroethylene (PTFE), polyvinyl alcohol (PVA), silicon rubber, SEBS rubber, etc., have been characterized for use in the MH electrode to obtain satisfactory mechanical strength; additives like carbon black will form a solid–gas interface to accelerate the oxygen recombination; a hydrophilic agent may generate a solid–liquid interface to enhance the water electrolysis, etc.

A significant improvement in electrode technology, for both MH and $\text{Ni}(\text{OH})_2$, allows improvement in the packing factor of the active materials without sacrificing the electrochemical efficiency, and in turn improves the NiMH energy density (see Table 1). Since 1991, NiMH batteries have become an important part, with growing potential, of rechargeable batteries and a well-developed new industrial domain, including manufacturing of raw materials and component parts around the NiMH batteries, has been established.

Challenges and Opportunities

Rapidly developing portable electronics demands even higher-performance batteries. Efforts to increase MH alloy capacity are a first step to meet the market demand for higher energy-density MH cells. Either discovering new alloys or further improving the existing AB_5 can achieve this. Theoretically, if the alloy capacity increases by 30% (i.e., to about 3000 mAh cm^{-3}), the cell energy density will increase approximately 10% by adjusting the number of active materials in both negative and positive electrodes. This increase would be without changing the cell design. Essentially, alloy chemistry determines the alloy hydrogen capacity. Metallurgical processing can improve the alloy capacity to some extent.

Obviously, price is always a major concern, and a low-cost battery is desirable. Improvement of cost performance of NiMH batteries depends heavily on the MH materials' cost. In 1990, the AB_5 alloy's price was about $\$40 \text{ kg}^{-1}$. Since then, the material price has gradually decreased. At present (2000), the alloy price is in the range of $\$15\text{--}20 \text{ kg}^{-1}$, a reduction of almost 60%. The major cause of the price reduction is worldwide industrialization. The demand for large-quantity alloys, standardization in misch metal composition and MH formulation, well-developed MH manufacturing technology, and stabilized raw material resources all contributed to the production efficiency, which makes the operating costs decrease dramatically. However, it is believed that further decreases in the material cost may mostly rely on modification of the alloy's chemical formula, based on a typical AB_5 formulation, $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$.

Intensive attempts in research and development on the AB_5 -type alloys, with new chemistries to reduce materials cost, are ongoing around the world. Misch metal, nickel, and cobalt are major components in the AB_5 alloys in terms of functioning role and cost. Reduction of one or all of the components will reduce the cost, but some technical approaches must be taken for performance compensation. To eliminate or partly reduce the cobalt content is a first attempt in this aspect. The major problem is poor cycle life, since cobalt is a key element in maintaining corrosion resistance.

Corrosion is an issue that needs to be resolved to improve NiMH performance under severe service environments. Alloys with high corrosion resistance, when subjected to electrochemical cycling, are desirable for improved performance. From the thermodynamic aspect, corrosion of AB_5 alloys in KOH under operating conditions is favorable. The free energy change of LaNi_5 oxidation, $\Delta G_{1/4} = -472 \text{ kJ mol}^{-1}$, is almost twice the enthalpy change of LaNi_5 formation (-127 kJ mol^{-1}), giving the alloy a strong driving force for oxidation in KOH solution. However, it has already been proven that it would not be possible to eliminate the causation, but it is technically possible to reduce the corrosion rate.

The improvement of corrosion rate can be directly transferred to longer cycle life. Particularly when the cell serves under high temperature, its corrosion becomes more severe. The corrosion rate improvement is also directly related to developing high-capacity and low-cost alloys, as seen from previous sections of this article. Taking advantage of the durable MH electrode, we can reduce the amount of excess MH materials that are used for charge reserve, making space for more active materials in the positive electrode to increase the cell energy density (assuming the corrosion improvement allows reduction of the excess MH alloy, which is for charge reserve).

The alloy chemistry is a determining factor in improving the alloy corrosion resistance. Aluminum substitution for nickel can improve the alloy's cycle life, probably due to its surface protection effect. The partial substitution of cobalt for nickel results in considerable improvement. Composition modification for the A side, such as the cerium element, significantly improves the chemical stability and in turn improves cycle life. This is ascribed to cerium's unique mixed $3/4$ valence state in the alloy, and the formation of a stable protective oxide layer on top of the MH particles.

Voltage performance is important for cell applications. Fig. 10 is a set of discharge profiles of a typical AB_5 electrode in a half-cell at different rates. The voltage was measured against a Hg/HgO reference electrode. From the curves, it can be seen at 5 C rate (1.5 A g^{-1}) that the electrode could deliver power with a midpoint voltage of about 0.56 V. Fig. 11 displays the electrode overpotentials (voltage drop) at various discharge rates. The overpotentials are obtained here using the voltage differences between the middle-point voltage of each discharge profile and the equilibrium potential, $E_{(1/4, 0)}$, of the same electrode at 50% DOD. A cell possessing high-rate capability can deliver power at high rate, or under normal operation, can benefit from less voltage drop.

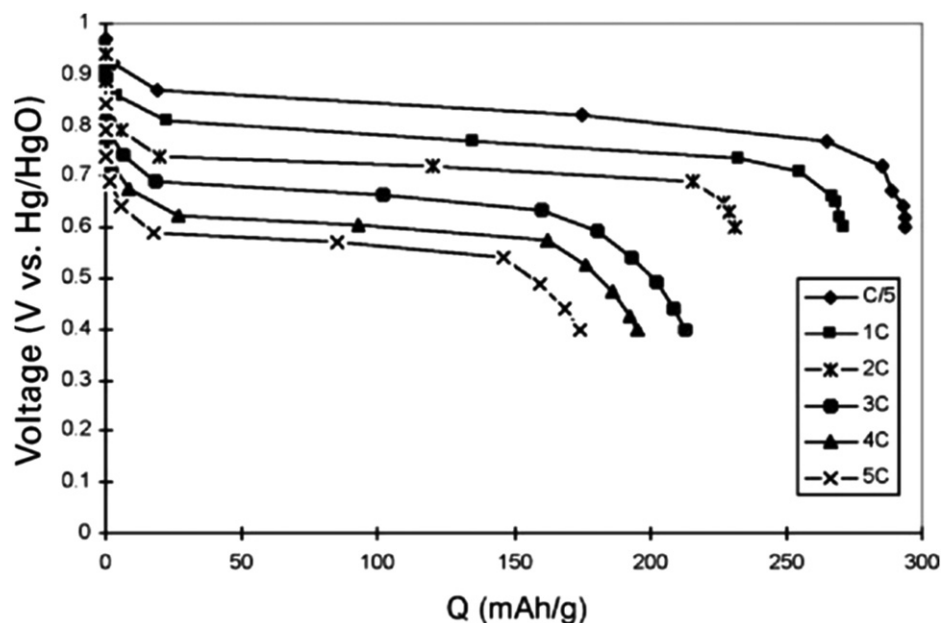


Fig. 10 Discharge profiles of a typical AB_5 electrode at different discharge rates at room temperature. The test was conducted in a half cell. The voltage was measured against Hg/HgO reference electrode.

High-rate capability is directly related to the electrode kinetics which can be caused by resistance resulting from three sources: charge-transfer reaction, mass-transport barrier, and internal contact resistance.

Charge-transfer reaction rates are governed by surface reactivity, which may be modified by the addition of oxides or a second phase. The mass-transport resistance may result from hydrogen diffusion in the bulk alloy, or from the diffusion of OH^- and H_2O through the electrolyte, particularly at higher rate. The hydrogen diffusion rate is an intrinsic property of MH materials and is related to enthalpy of formation. MH alloy's diffusion constant may be in a range from 10^{-8} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ (Willems, 1984; van Rijswijk, 1978), depending on the nature of the alloys and the measuring technique. For a given alloy, its hydrogen diffusion constant is a fixed number at a certain temperature. However, the particle size can play a role due to the change of diffusion distance.

If we take the MH as spherical particles, for a cell containing 10 g of MH, only 70% of the MH capacity participates in the discharge reaction (assuming 30% charge reserve). Fig. 12 displays the relationship of cell rate capability with diffusion rate and particle size, based on the assumption that the cell rate was controlled by hydrogen diffusion. Two diffusion constants were taken in the prediction model: one is $10^{-9} \text{ cm}^2 \text{ s}^{-1}$, the other $10^{-8} \text{ cm}^2 \text{ s}^{-1}$. Of course, the MH particle will be broken down with continuous cycling. However, at least the rate capability on the early charge/discharge cycling can be enhanced by using smaller particles. To obtain a rate of 40 A, if the diffusion constant is $10^{-9} \text{ cm}^2 \text{ s}^{-1}$, the particle size should be no larger than 15 mm, while for $10^{-8} \text{ cm}^2 \text{ s}^{-1}$, 40 mm particles are enough. In addition, the smaller particle size also provides larger surface area which definitely increases reactivity.

Contact resistance is related to many factors. Various authors systematically analyzed the electrode reaction using electro-chemical impedance spectroscopy. It was found that the contact resistance consisted of three parts: electrolyte resistance, contact resistance between the substrate and MH alloy, and contact resistance between the MH particles. The contact resistance between the MH and substrate and between the particles significantly increased with cycling, which is obviously related to the alloy degradation products of the oxides. The structure and thickness of the electrode, the alloy corrosion resistance, the kinds of additives, and the nature of binder materials all contribute to the resistance. They suggested that copper coating could significantly improve the electrode contact resistance.

Applications

The NiMH battery can be designed in a variety of forms, such as button cells, prismatic cells, and cylindrical cells, and in different sizes. The characteristics of the NiMH battery present opportunities for use over a wide range, and it will become one of the leading rechargeable battery systems.

Because of the same voltage value as the NiCd battery, all devices using NiCd can adopt NiMH as their power sources. As a result, the NiMH battery is increasingly used in a wide range of consumer electronic devices, such as cellular phones, camcorders, shavers, transceivers, computers, and other portable applications. Another niche market suitable for NiMH battery is power tools, which require high power discharge capability over a wide temperature range.

The NiMH battery has attractive energy density, high power capability, and good cycle life, all of which make the NiMH a competitive choice for EV and HEV applications, which may become a very important market for rechargeable batteries in the first decade of the twenty-first century. The commercialization of HEV cars by Toyota, Honda who use NiMH batteries, the desire for improving environments, and the concerns of fossil fuel resources have fueled a worldwide surge in the development of various battery-assisted vehicle

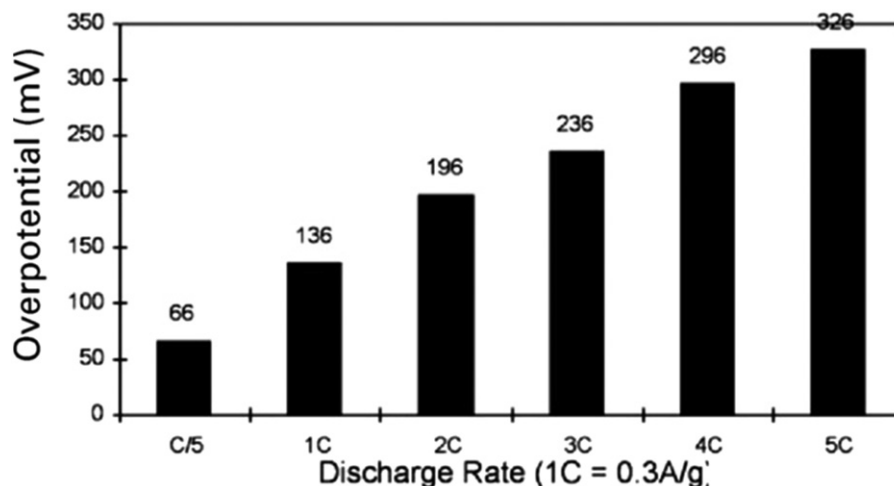


Fig. 11 The overpotentials of the MH electrode at different discharge rates.

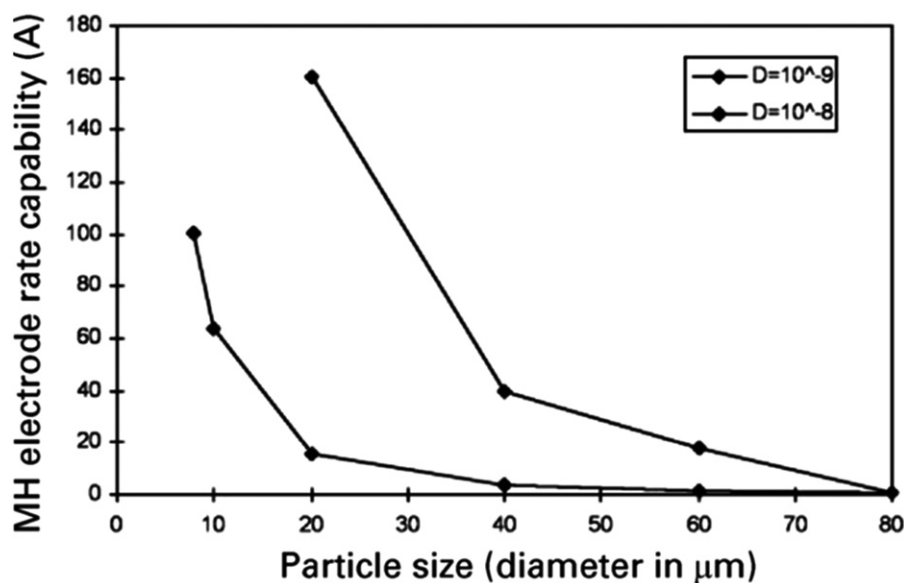


Fig. 12 Prediction correlation between the particle size and the electrode rate capability, assuming the reaction is controlled by hydrogen diffusion.

applications. A major issue for users of portable electronics, EV and HEV applications, is the estimate of the battery's state of charge (SOC), which can translate useful information necessary for managing the battery system, such as how much energy is stored in the battery, how much runtime is left before the need for recharging, what recharge or discharge rate can be applied, etc.

Therefore, a kind of 'fuel gage' has been expected, and a variety of schemes for measuring battery SOC have been suggested. In general, experience with NiMH cells indicates that, due to the flatness of the voltage plateau under normal conditions, voltage sensing may not be used to accurately determine the SOC. However, coulometry is a good technique for sensing the SOC. With careful initial calibration, appropriate compensation for environmental conditions, sophisticated charge-flow tracking, and estimation of self-discharge losses, predictions of SOC with moderate accuracy can be obtained.

The high-rate discharge and fast recharge capability of the NiMH battery also make it a candidate to combine with fuel cells, solar cells, and other batteries or internal combustion engines to handle peak loads or provide power when the prime power source is not adequate or not available.

Lithium-Ion Rechargeable Batteries

Rapid development of new technologies, such as portable consumer electronics and electric vehicles, has generated the need for batteries that provide both high energy density and high-power capability. Considering thermodynamic reasons, lithium shows a

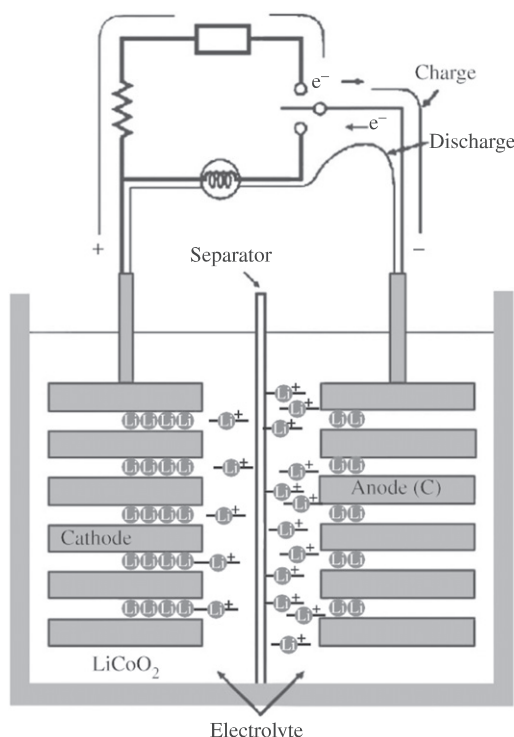


Fig. 13 Schematic diagram of the principles of a Li-Ion rechargeable cell (after Nishi, Y., 1998. Performance of the first lithium ion battery and its process technology. In: Wikiphara, W., Yamamoto, O. (Eds), *Lithium Ion Batteries*. New York: Wiley-VCH, pp. 181–198).

chemical and electrochemical behavior which favors it for selection as an anode material to be used in high-energy and high-power batteries.

Lithium metal has a very large theoretical capacity of 3860 mAh g^{-1} , in contrast to the value of 480 mAh g^{-1} for cadmium and 372 mAh g^{-1} for AB_5 metal-hydride alloy (Murphy and Caride, 1979). Lithium is much more electropositive than hydrogen, with high standard potential (Li: -3.01 V ; Cd: -0.4 V) which allows the realization of significantly higher voltage. In addition, lithium possesses a low density and hence low electrochemical equivalent weight (Li: 0.259 gA h^{-1} ; Cd: 2.10 gA h^{-1} ; AB_5 : 3.30 gA h^{-1}).

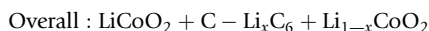
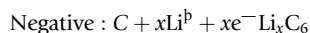
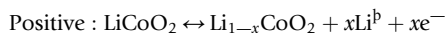
During the past decades lithium rechargeable batteries, using lithium metal as the anode and intercalation compounds as the cathode, have been intensively studied. The difficulties associated with the use of metallic lithium stem from the changes that occur after repetitive charge–discharge cycling and its reactivity with the electrolyte. The thermal stability of lithium metal foil in many organic electrolytes are good, with minimal exothermic reaction occurring up to temperatures near the melting point of lithium (180°C). However, during recharge, lithium is electroplated onto the metallic lithium electrode, and forms a more porous deposit with a larger surface area than the original metal, which significantly increases its reactivity and lowers the thermal stability limit of the system. Therefore, the cells become increasingly sensitive to abuse as they are cycled. Another disadvantage is the short cycle life.

This happens because lithium is not thermodynamically stable in the organic electrolytes and the surface of the lithium is covered with a film of the reaction products between the lithium and the electrolyte. Every time the lithium is stripped and replated during the discharge and charge, a new lithium surface is exposed and then passivated with a new film, consuming lithium. In order to obtain a reasonable cycle life, a three- to five-fold excess of lithium is required, which increases safety challenges. The formation of dendritic lithium at the interface of Li anode and the electrolyte can be suppressed by depositing amorphous carbon coating onto the metallic lithium foil by magnetron sputtering. The magnetron sputtering overcomes the complication in the conventional fabrication and this is most suitable for industrial production. Thick coating of carbon on surface improves the electrochemical properties of lithium batteries and increases the life cycle. However, larger the thickness of coating, higher is the impedance for lithium transfer (Zhang *et al.*, 2014). To overcome these problems, a safer approach is to replace lithium metal with a lithium intercalation compound, usually a carbon one (Lazzari and Scrosati, 1980). In 1990, the so-called ‘rocking-chair’ or ‘lithium-ion’ (Li-Ion) battery was put on the market by Sony Energetic Inc. (Nishi, 1998). In the Li-Ion battery, lithium ions swing between the carbon anode and the layered, highly oxidizing cathode through an organic liquid electrolyte dissolving inorganic lithium salt, like a rocking chair rocking from side to side. The principal concept is based on the intercalation reaction and is rather different from conventional secondary batteries which are based on chemical reactions.

A well-known typical Li-Ion cell, in which a lithiated carbon intercalation material (Li_xC_6) is used as the negative electrode, a lithiated transition metal intercalation compound (lithium cobaltite, LiCoO_2) is used as the positive active material, and an aprotic organic solution (lithium salt LiPF_6 dissolved in mixed propylene carbonate (PC)–ethylene carbonate (EC) solvent) as the electrolyte, is expressed as follows (Scrosati and Megahed, 1993):



The reactions at the electrodes and the overall cell reaction can be represented by the following equations:



Lithium ions move back and forth between the positive and negative electrodes during charge and discharge. At the negative electrode, the electrochemical process is the uptake of lithium ions during charge and their release during discharge, rather than lithium plating and stripping. As metallic lithium is not present in the cell, Li-Ion cells are less chemically reactive and have a longer cycle life than the cells containing metallic lithium. The reaction mechanism of the Li-Ion cell is shown graphically in Fig. 13.

Lithiated carbon is air-sensitive. In practice, the Li-Ion cell is manufactured in a fully discharged state. The fabrication procedure is based on the use of a lithium-rich intercalation compound as the cathode (positive electrode). The cell is assembled by coupling this lithium-rich or lithium source cathode compound with a lithium-accepting anode (negative electrode). The cell is 'activated' by charging, which transfers lithium ions from the cathode to the anode which is thus lithiated. Most powdered intercalation compounds are pyrophoric when loaded with lithium. However, lithium will not deintercalate to react with air or moisture if it is sufficiently bound in the intercalation compound. Lithium intercalation compounds such as $\text{Li}_{1-x}\text{CoO}_2$ (0.0 < x < 0.5), LiNiO_2 (0.0 < x < 0.5), and LiMn_2O_4 (0.0 < x < 0.85), are generally air stable when the chemical potential is less than 3.6 eV.

The specific energy density of a Li-Ion battery with high discharge voltage (3.6 V) is nearly twice as high as the NiCd battery, and about 60% higher than NiMH batteries. In addition, the Li-Ion battery has demonstrated excellent cycle life and much-improved intrinsic safety.

Anode Active Materials – Carbon

Carbon materials can reversibly accept and donate significant amounts of lithium without affecting their mechanical and electrical properties. The lithiated carbon also has a Fermi energy only about 0.5 eV below that of lithium metal. Therefore, in the Li-Ion cell, carbon is used for the anode instead of metallic lithium, and thus the electrochemical cell will have almost the same open-circuit voltage as one made with metallic lithium.

The carbon anode is a key component of the Li-Ion battery, and various carbon materials ranging from graphite to amorphous carbon have been proposed. Graphite has a layered structure. The graphite can be reduced by electrochemical intercalation with lithium in an aprotic organic electrolyte containing lithium salts to form LiC_6 with a capacity of 372 mAh g⁻¹. The formed LiC_6 can be electrochemically oxidized by lithium deintercalation. Graphite is a passable material as an anode; however, some drawbacks have been observed, including limitation of capacity, anode bulging, and poor cyclability. From the viewpoint of materials science as well as battery applications, carbon attracts much interest because of its variety of structures. It is the structure that plays the most important role in electrochemical performance and makes the diverse characteristics of the carbon.

Carbons bind themselves together by sp^3 , sp^2 , and sp hybrid orbitals, forming many kinds of organic compounds. However, the carbon materials discussed here are mainly built up by sp^2 bonding (Tran *et al.*, 1995). Repeating sp^2 bonding forms a large network of 6-ring structures leading to a two-dimensional graphene sheet. The stacking order of these graphene sheets is important; van der Waals forces bind the sheets together forming layered crystalline structures. The ideal stacking order of graphite has two patterns: the carbon positioned in ABAB pattern has hexagonal symmetry with space group $P6_3/mmc$, while the ABCABC pattern has rhombohedral symmetry with $R3m$. Fig. 14 schematically displays the crystal structure of hexagonal graphite showing the AB graphene layer stacking sequence and the unit cell.

Natural graphite usually comprises these two crystal structures, but the rhombohedral phase is below 3–4%. For graphite, the weak van der Waals force between layers enables the planes to slide easily. Practical carbon materials generally have varying degrees of stacking faults resulting in carbon atoms deviating from regular positions, and periodic stacking is no longer maintained. In general, carbon materials capable of lithium intercalation can be roughly divided into graphitic carbon and nongraphitic carbon. Graphitic carbons are carbonaceous materials of layered structure but with some structural defects (turbostratic orientation). The graphitic carbons are commonly called 'graphite' regardless of stacking order, since perfectly stacked graphite crystals are practically not available.

For nongraphitic carbonaceous materials, carbon atoms are arranged in a planar hexagonal network but without the crystallographic order in the C-direction of the graphite structure. Nongraphitic carbons are mostly prepared by pyrolysis of organic polymer or hydrocarbon precursors (Pierson, 1993). It is also common to separate the nongraphitic carbon into 'graphitizing' and 'nongraphitizing' carbons. Graphitizing carbons can be easily converted to graphite, which has an orderly layered structure, by calcinations at temperatures as high as 3000°C, and lithium can intercalate only into the spacings between the layers to form LiC_6 . Graphitizing carbon, which is also called 'soft carbon,' has a slightly disordered structure. On the other hand, nongraphitizing carbon materials consist of randomly oriented small crystallites, and this type of carbon cannot be converted to graphite by calcinations even at 3000°C, which is the reason it is called 'hard carbon.' We will see the difference between the 'soft carbon' and the 'hard carbon' in the following section.

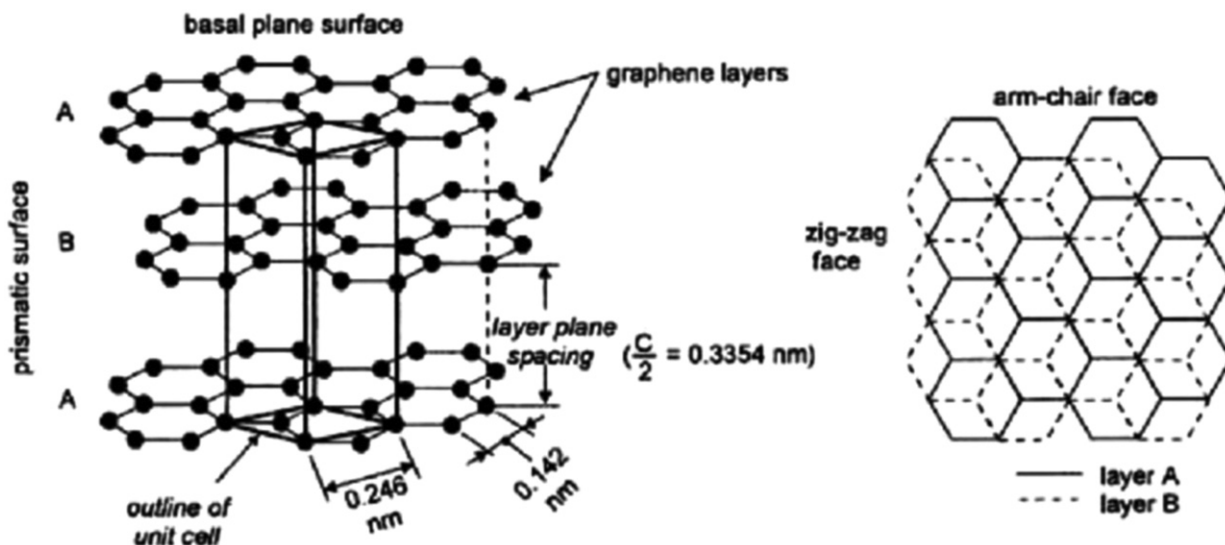
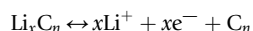


Fig. 14 Left: schematic drawing of the crystal structure of hexagonal graphite showing the AB graphene layer stacking sequence and the unit cell. Right: view perpendicular to the basal plane of hexagonal graphite (after Winter, M., Besenhard, J.O., 1999. Lithiated carbon. In: Besenhard, J. O. (Ed.), Handbook of Battery Materials, vol. 406. New York: Wiley-VCH.).

Charge/Discharge Mechanisms of Carbon Anodes

The reversible insertion of mobile lithium guests into the structure of a solid carbon host is commonly referred to as 'intercalation.' In general, the designation of an insertion reaction by the term intercalation involves the condition that the host matrix units mostly retain their integrity with respect to composition and structure during the intercalation and deintercalation processes. Electrochemical intercalation reactions are confined to coupled electron/ion transfer ('mixed condition') reactions. For lithium intercalation into a carbon electrode from an appropriate Li⁺-containing electrolyte, this means that due to the cathodic reduction of the carbon, the lithium guest ions penetrate into the carbon host, forming a lithium/carbon intercalation compound, as illustrated in Fig. 15.

The corresponding negative charges are accepted into the carbon host lattice. The reversibility of the intercalation reaction can be checked by subsequent anodic oxidation of LiC_n, i.e., by removal or deintercalation of Li:



The host/guest charge transfer, although not complete, usually leads to an increased electron density in the conductivity band of carbon and thus to an increase of the in-plane electronic conductivity by several orders of magnitude. Therefore, the carbon intercalation compounds are occasionally named 'synthetic metals.'

It was concluded that soft carbons always have at least two mechanisms to accommodate lithium (Maubuchi *et al.*, 1995). In the potential ranges from 0 to 0.25 V, lithium is intercalated into graphitic parts and the capacity can be described as follows:

$$C_{0.25\text{V}} = \frac{1}{4}372 \times P_1 (\text{mAh g}^{-1})$$

where P_1 is a fractional ratio of perfect graphite stacking. The maximum capacity is 372 mAh g⁻¹ when $P_1 = 1$ for graphite. In the potential region above 0.25 V, the intercalation mechanism changes and depends on heat-treatment temperature. At lower heat-treatment temperatures, for example, at 1000°C, the soft carbon electrode shows capacity larger than 372 mAh g⁻¹. This is attributed to the existence of micropores or 'cavities' formed between crystallites. It is proposed that lithium intercalates into the graphite layers and the cavities at the same time during charge; in discharge, lithium is first deintercalated from the layers, and then extracted from cavities.

This mechanism is illustrated in Fig. 16. In the case of hard carbon, lithium can be electrochemically charged into ultramicropores (with a diameter of 0.7–0.8 nm) as well as the layers of crystallites themselves. The ultramicropores are probably able to trap lithium in clusters therefore resulting in higher capacity, up to 600 mAh g⁻¹, which exceeds the stoichiometric capacity of LiC₆ (Ishikawa *et al.*, 1994). The hard carbons are made up of single graphene sheets which are arranged like a 'house of cards' (Xue and Dahn, 1995). On charging, intercalated lithium is adsorbed onto both sides of each of the graphene sheets, leading to high lithium capacity. Discharge curve profiles of Li-Ion cells are illustrated in Fig. 17. The sloping discharge profile is characteristic of the Li-Ion cells using hard carbon materials, compared to the flatter discharge profile of the cells using graphite.

In addition, it is observed that the hard carbon is very stable during charge/discharge cycles and exhibits excellent cycle performance. During charge and discharge cycles, graphite and soft carbon repeatedly expand and shrink. This repeated expanding and shrinking between layers, resulting in rapid capacity fade during cycling, damages the graphite structure. Furthermore, this expansion causes deformation of electrodes. In contrast, hard carbon has broader spacing between layers (over 0.372 vs. 0.335 nm for graphite) and suffers less damage during the cycling. Hard carbon therefore becomes a powerful candidate as a practical anode material.

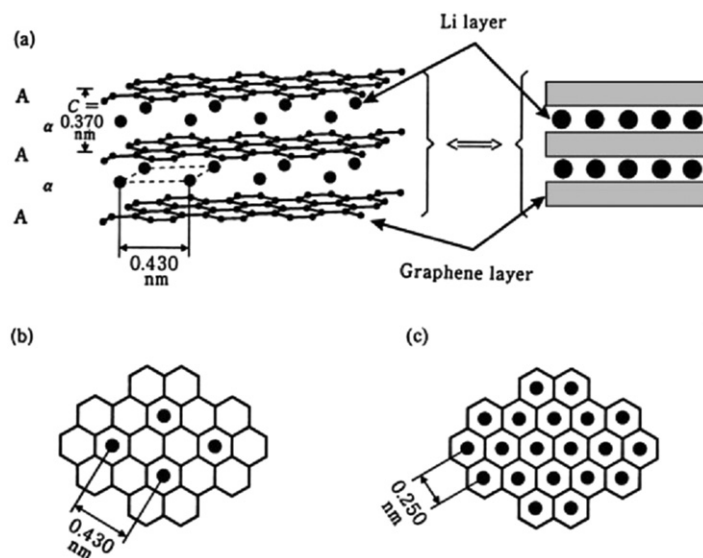


Fig. 15 (a) Left: schematic showing graphite AA-layer attacking and lithium intercalate aa interlayer ordering. Right: showing simplified schematic representation. (b) In-layer ordering model of LiC_6 . (c) In-layer ordering model of LiC_2 (after Winter, M., Besenhard, J.O., 1999. Lithiated carbon. In: Besenhard, J.O. (Ed.), Handbook of Battery Materials, vol. 406. New York: Wiley-VCH).

Surface Reactions of a Carbon Anode

During the first electrochemical intercalation of lithium into the carbon, some lithium is irreversibly consumed and a significant amount of capacity cannot be recovered in the following discharge. This irreversible capacity, which depends on the electrolyte solution and the type of carbon material, can be explained on the basis of the reduction of electrolyte solution and the formation of a passivation film at the Li_xC interface.

The anode/electrolyte interphase, which is named the 'solid-electrolyte interphase' (SEI) (Winter and Besenhard, 1999), plays a key role in Li-Ion batteries. It determines the safety, power capability, lower-temperature performance, faradaic efficiency on charge, the cycle life, and the irreversible capacity loss in the first charge cycle. The irreversible decomposition of organic solvents is one of the major problems regarding the carbon anode, which results in irreversible losses. A passivation surface layer is always formed in any electrolyte system and the characteristics of the formed film greatly affect electrode behavior. Prior to lithium intercalation, charge current was consumed forming a surface passivation film. In the case of PC electrolyte, the film produced by cathodic decomposition of PC appears to be quite porous and cannot cover the surface well, therefore solvated lithium ions easily intercalate from the uncovered part at a potential positive to lithium deposition (B 0.8 V vs. Li/Li^+).

This causes exfoliation of graphite sheets and damages the reversible behavior of the anode. If the electrolyte consists of EC and EC-based solvents, the film is formed uniformly over the surface, completely screening the graphite from the electrolyte; thus, further decomposition is prevented and the capacity loss is limited to a negligible level. In addition, this surface film is a good lithium conductor and lithium ions can migrate through it without solvent molecules. It can be seen that the stability of the solvents determines the electrochemical behavior of a graphite anode. The long-term stability of the anode clearly depends on the property of the protective surface film.

Many efforts have been made to improve anode performance of carbon materials. It is important to reduce the irreversible decomposition of electrolyte and enhance the reversible capacity. Texture control can, to some degree, change the electrical conductivity of the electrode, the active surface area, the porosity, and the structure of the interface between electrode and electrolyte, and therefore improve the electrochemical performance of the carbon anode (Peled, 1979). The effects of doping with phosphorus, boron, silicon, and nitrogen have been studied and it was found that such doping may improve capacity, coulombic efficiency, and cycle life (Imanish *et al.*, 1993).

For operation under heavier loads, further improvement of the carbon anodes is essential. There is strong interest in developing new anode materials to replace the carbon for better performance. A lithium cell with the trademark Stalion announced by Fujifilm Celltec Co. has attracted significant interest (Weydanz *et al.*, 1994), because it provides a higher energy density, as shown in Fig. 18, a promising cycle life, and a higher power density. The improvement is achieved by replacement of the carbon anode with an amorphous tin-based composite oxide (TCO or ATCO).

The specific energy capacity of the Li-Ion systems depends largely on the type of carbon materials, the lithium intercalation efficiency, and the irreversible capacity associated with the first charge process. It has been found that coke-type carbon, having physical properties such as ash content 0.1%, surface area $10 \text{ m}^2 \text{ g}^{-1}$, true density 2.15 g cm^{-3} , and interlayer spacing 43.45 Å, is suitable for Li-Ion systems. These types of carbon materials can provide about 185 mAh g^{-1} capacity ($\text{BLi}_{0.5}\text{C}_6$). By controlling the temperature of the heat treatment, carbon materials having specific properties such as density and interlayer spacing can be

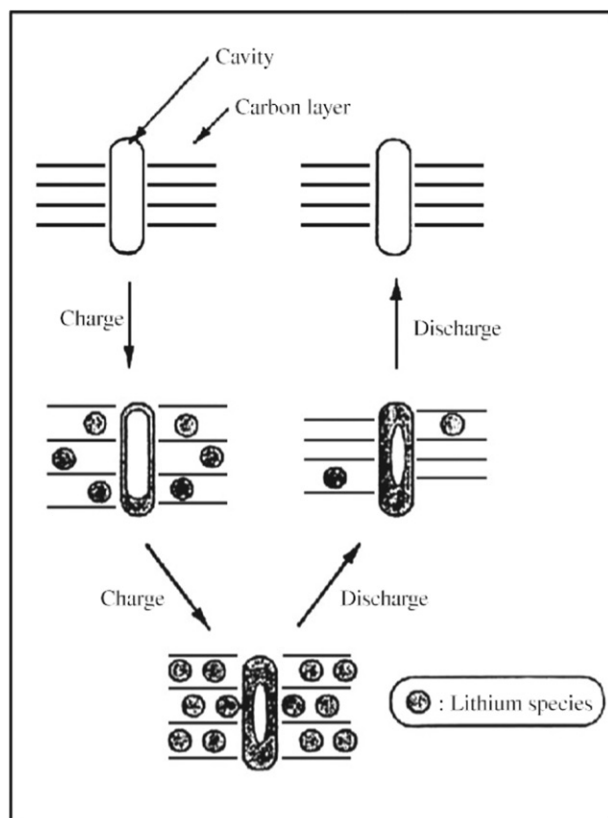


Fig. 16 Schematic illustration of the charge–discharge mechanism of a carbon anode involving cavities (after Maubuchi, A., Tokumitsu, K., Fujimoto, H., Kasuh, K., 1995. Charge – discharge characteristics of mesocarbon microbeads heat treated at different temperatures. *J. Electrochem. Soc.* 142, 1041–1046.).

prepared. A nano composite anode material of silicon/graphite/MultiValved carbon NanoTubes (MWNTs) prepared by ball milling method exhibits a discharge capacity of 2274 mAh g^{-1} in first cycle and reversible capacity of 584 mAh g^{-1} after 20 charges/discharge cycle. This is higher when compared to silicon/graphite composite. The silicon particles were homogenously embedded into the ‘lamellar structures’ of flaked graphite particles and further wrapped by MWNTs network. The high degree of resiliency and good electric conductivity of MWNTs network mainly contributed to the enhancement of overall discharge capacity and cyclability of the silicon/graphite/MWNTs composite anode material (Zhang, *et al.*, 2006).

The capacity of the anode materials can be increased more than four times using Tin dioxide (SnO_2) nanocrystals encapsulated in 3-D graphene framework. A stable capacity of about 1050 mAh g^{-1} is maintained for 200 cycles at current density of 0.2 A g^{-1} . For higher current density of 5 A g^{-1} , a reversible capacity of about 491 mAh g^{-1} was achieved with this electrode. The 3D architecture has large free space, which can tolerate the drastic volume change during lithium-ion insertion. Also, this anode material has long cycling stability and high-rate capability proved as high-performance electrode for Lithium batteries (Xue *et al.*, 2015).

The transfer resistance of lithium ion can be reduced by using composite anode material of Si/reduced graphene oxide (rGO) aerogel. This composite electrode gives the high specific capacity and cycling stability. The composite is fabricated by steam etching of Si/rGO aerogel. The silicon nano particles are encapsulated in rGO sheet with nano-holes to form a 3D stable porous network structure which increases the specific surface area. The porous structure helps the entire electrode to maintain high conductivity and facilitate the lithiation of Si nanoparticles (Tang *et al.*, 2015).

Cathode Active Materials – Lithiated Oxides

There is a wide range of choice for materials that can be selected for the positive electrode of Li-Ion rechargeable batteries. However, a number of factors have to be considered in choosing the intercalation compound, such as reversibility of the intercalation reaction, electronic conductivity, free energy of reaction with lithium, cell voltage window, variation of the voltage with the state of charge, and availability and cost of the compound.

Compared with lithium metal batteries, the cathode materials suitable for Li-Ion batteries are highly oxidizing compounds which may compensate for the loss in cell potential at the anode (Pistoia, 1994). The best cathodes for Li-Ion rechargeable batteries are those where there is little bonding and structural modification of the active materials during the charge–discharge reaction. Candidate cathode materials include layered compounds with the general formula LiMO_2 (Thackeray, 1999), such as.

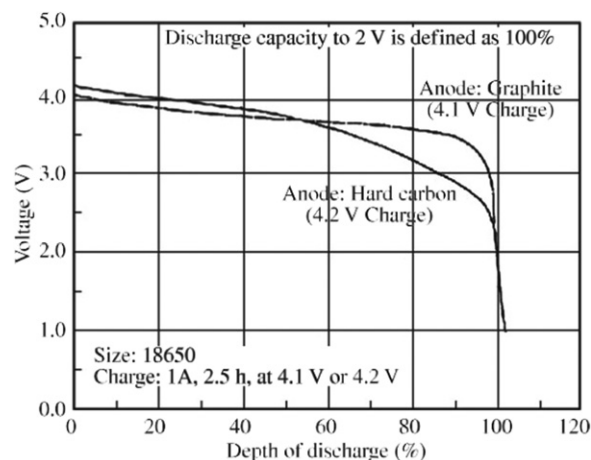


Fig. 17 Discharge curve profiles of Li-Ion cells with graphite and hard carbon anodes (after Nishi, Y., 1998. Performance of the first lithium ion battery and its process technology. In: Wikiphara, W., Yamamoto, O. (Eds), *Lithium Ion Batteries*. New York: Wiley-VCH, pp. 181–198).

LiCoO_2 , LiNiO_2 , and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$. In the ideal layered LiMO_2 structure, the Li and the M^{3+} ions occupy octahedral sites in alternate layers between cubic close-packed oxygen layers as shown in Fig. 19. The layered metal oxide framework provides a two-dimensional interstitial space, which allows easy removal of the lithium ions. The intercalation and deintercalation of the lithium ion for the layered structure compounds are represented by the following equation:



When the Li/LiMO_2 cell is cycled over the limited composition range $0 \leq x \leq 0.5$ in $\text{Li}_{1-x}\text{MO}_2$, rechargeability and charge retention are good. However, the rechargeable capacity fades rapidly for deep charge and discharge cycles, i.e., for $x > 0.5$. Discharge curve profiles of lithium-ion cells with layered LiMO_2 cathodes are displayed in Fig. 20.

The compound LiCoO_2 is an attractive positive electrode because it has a stable structure which is easy to prepare with the ideal layered configuration. Therefore, practically, the maximum capacity of LiCoO_2 is about 125 mAh g^{-1} based on weight of LiCoO_2 . LiNiO_2 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ have rechargeable capacities more than 150 mAh g^{-1} . It is difficult to prepare large and reproducible LiNiO_2 batches with the ideal layered structure. It was also observed that extensively delithiated (charged) $\text{Li}_{1-x}\text{NiO}_2$ electrodes are less stable than $\text{Li}_{1-x}\text{CoO}_2$ electrodes and its thermal behavior is a threat to safety (Dahn *et al.*, 1991). The drawbacks of the LiNiO_2 electrodes can be partly overcome by using cobalt-substituted $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ or aluminum-substituted $\text{LiAl}_{0.25}\text{Ni}_{0.75}\text{O}_2$. A very promising cathode material is the three-dimensional compound which is represented by LiMn_2O_4 (Thackeray, 1999). Fig. 21 displays the spinel framework structure. The intercalation and deintercalation of the lithium ion for the spinel structure compounds is expressed as follows:



The reversible value of x is as high as 0.85 and its reversible capacity is 135 mAh g^{-1} . The manganese-based materials offer the following advantages: better structural stability, lower cost resulting from the natural abundance of manganese, and lower toxicity.

For practical applications, considering the high cost of cobalt or nickel, LiMn_2O_4 spinel compounds are more desirable cathode candidates for Li-Ion batteries.

Electrolytes

The magnitude of the open-circuit voltage along with other performance issues (such as theoretical energy density, high-rate capability, etc.) is constrained not only by the electrochemical potentials (the Fermi energy) of the anode reductant (m_A) and the cathode oxidant (m_C), but also by the chemistry of the electrolyte. For example, it is the energy gap E_g between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of a liquid electrolyte that determines the thermodynamic stability. The selection of electrolyte for the Li-Ion batteries is critical.

The ‘electrolyte’ here actually consists of a solvent and a lithium salt. Nonaqueous organic electrolyte solutions are widely used in commercial Li-Ion batteries. The electrolyte solution must possess a wide potential window (0–5 V), low vapor pressure, good ionic conductivity, and compatibility with other cell components. The solvents should be aprotic so as to be stable at fairly low potentials, and so that they do not react with metallic lithium, but should have high polarity in order to dissolve lithium salts, giving high ionic conductivity.

Low values of both melting point and boiling point of the solvent are preferred, since they directly relate to the operating temperatures of the battery system and reflect the physical chemistry of the solvent such as the molecular structure and intermolecular forces. The relative permittivity and viscosity of the solvent are the most important properties that determine the ionic

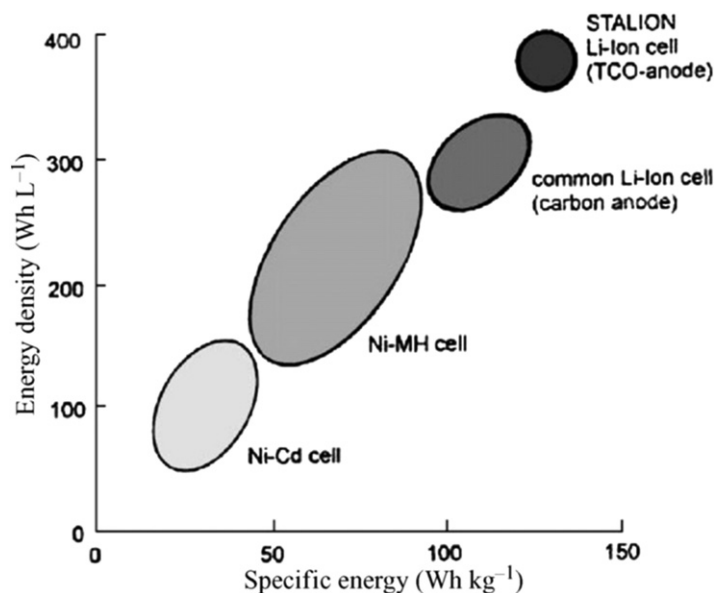


Fig. 18 Energy density comparison for NiCd, NiMH, and Li-Ion rechargeable batteries. TCO: amorphous tin-based composed oxide (after Weydanz, W.J., Way, B.M., van Buuren, T., Dahn, J.R., 1994. Behavior of nitrogen-substituted carbon (N_2C_{1-z}) in $Li/Li(N_2C_{1-z})_6$ cells. J. Electrochem. Soc. 141, 900–907).

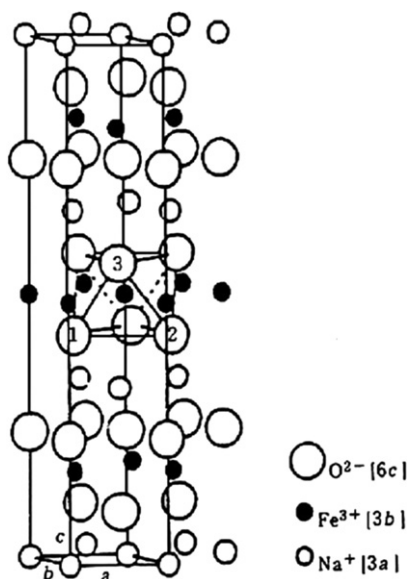


Fig. 19 The structure of layered α - $NaFeO_2$, prototype of $LiCoO_2$, and $LiNiO_2$ (after Thackeray, M.M., 1999. Materials for alkali metal batteries. In: Besenhard, J.O. (Ed.), Handbook of Battery Materials. New York: Wiley-VCH, pp. 293–317.).

conductivity of the electrolyte solution (Li and Currie, 1997). Lithium salts with monovalent anions are preferred for the battery electrolyte because of the higher extent of dissociation of the salt and higher mobility of the resulting ions.

The most popular aprotic organic electrolyte solutions are made by dissolving very ionic lithium salts such as $LiClO_4$, $LiBF_4$, $LiAsF_6$, or $LiPF_6$ in empirically optimized mixtures of propylene carbonate (PC), ethylene carbonate (EC), or dimethyl carbonate (DMC). Voltages approaching 4.5 V have been sustained in an electrolyte of $LiPF_6$ in a 1:2 DMC: EC mixture. However, these organic liquid electrolytes generally have conductivities of 10^{-2} S cm^{-1} at most, about two orders of magnitude lower than aqueous electrolytes (8×10^{-1} S cm^{-1} of H_2SO_4 for lead-acid batteries, 5×10^{-1} S cm^{-1} of KOH for alkaline systems). Therefore, many efforts have been attempted to improve the ionic conductivity and other performance of the organic electrolyte solutions. Polymer electrolyte is an alternative to the liquid electrolyte, and is formed by incorporating lithium salts into polymer matrices, followed by a casting procedure to obtain a thin film. By proper control of the conditions of the synthesis, it is possible to make membranes with a thickness between 20 and 100 μm . A thinner polymer film (5 μm) with acceptable conductivity, adequate

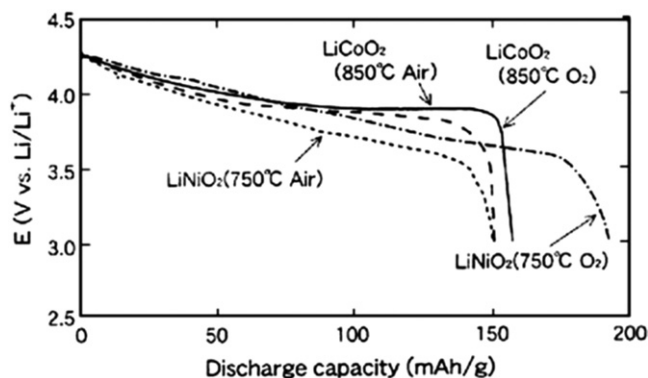


Fig. 20 Discharge curve profiles of Li-Ion cells with layered LiMO_2 cathodes.

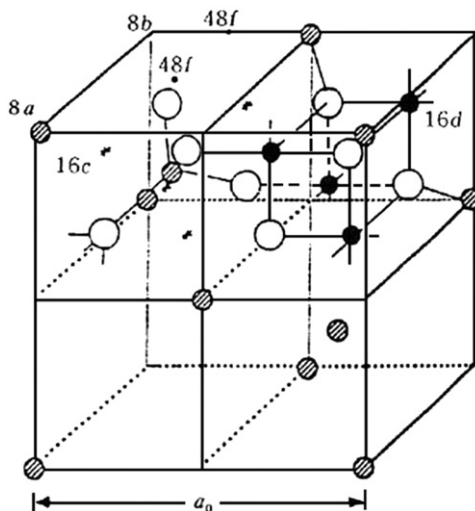


Fig. 21 The spinel structure of a LiMn_2O_4 -type compound (after Thackeray, M.M., 1999. Materials for alkali metal batteries. In: Besenhard, J.O. (Ed.), Handbook of Battery Materials. New York: Wiley-VCH, pp. 293–317).

mechanical strength, and electrochemical stability, is an ideal material as an electrolyte. The polymer membranes can be used as both electrolyte and separator.

These electrolytes are less reactive with lithium and should enhance the battery's safety, eliminate the possibility of electrolyte leakage, and provide good adhesion to the electrode, thus ensuring good interfacial contact. Batteries with polymer electrolytes can be placed in metallized plastic bags allowing the construction of batteries with customized shapes. However, due to the slow ionic transport within the polymer structure, these solid electrolytes have ionic conductivities of below $10^{-4} \text{ S cm}^{-1}$ at 20 °C, much lower than the liquid one, and, practically, the battery requires higher temperatures in order to obtain enough conductivity for acceptable performance.

Another class of polymer electrolytes called 'gel' electrolytes are developed by the addition of a polymer or fumed silica into the liquid electrolyte or by cross linking of a dissolved monomer (Abraham *et al.*, 1995). Conductivities as high as $10^{-3} \text{ S cm}^{-1}$ at 20 °C were achieved. However, their chemical stability and reactivity with lithium should be improved for practical applications.

Separators for Li-Ion Batteries

All the requirements for separators used in alkaline storage batteries, such as mechanical strength and chemical stability, should be provided for Li-Ion batteries. The separator should prevent migration of particles of B10 mm between electrodes, so the effective pore size should be less than 1 mm. During winding, small pieces of electrode material may come off and be forced into the separator by winding tension. The separator must not be punctured; otherwise, the battery will be shorted. Generally, a Li-Ion battery is used at a C rate, and it may require a current density of $0.5\text{--}3 \text{ mA cm}^{-2}$ depending on cell design. For high-rate applications, the current density will be much higher. The electrical resistance of the separator should not limit battery performance under any circumstances. It is also regulated (Underwriters Laboratories, 1993) that the battery be able to withstand a short circuit without fire or explosion.

Table 2 Comparison of NiCd, NiMH, and Li-Ion battery systems

System	Energy density		Power		Cycle life ^b	Self-discharge
	Wh kg ⁻¹	Wh L ⁻¹	Wk. g ⁻¹	W L ⁻¹		
NiCd	50	90	250	600	41,200	30 ^c
NiMH ^a	65	160	200	475	41,200	30 ^c
Li-Ion ^a	110	165	750	1600	4600	10 ^d

^aEstimated from Anderman *et al.* (2000).^bAt room temperature 100% DOD to 80% of initial capacity.^cAt room temperature for 30 days.^dAt room temperature for 90 days.

A positive temperature coefficient (PTC) device (called a Polyswitch) has been used for external short-circuit protection. The PTC device is placed in series inside the cell. Its resistance increases by orders of magnitude at high currents and resulting high temperatures, and suddenly jumps to infinite value at a certain temperature level (so-called trip temperature; generally, 100°C).

As soon as the temperature reaches the trip value at external shortage, the short-circuit current is stopped due to the infinite electrical resistance, preventing thermal runaway of the cell. However, in the case of an internal short, for example, if the positive tab comes loose and connects to the interior of the negative metal can, the PTC will not respond quickly enough. During overcharging, the PTC may not be activated at low current. In these cases, it is an advantage that a separator provides safety functions and prevent thermal runaway by fusing itself. In fact, the separator could act as a fuse. That is, the impedance of the separator increases by two or three orders of magnitude due to an increase in cell temperature, and melts down so that it closes its pores and effectively stops the current flow between the electrodes.

It is found (Yu *et al.*, 1994) that a trilayer structure of PP/PE/PP Celgard microporous membranes offers unique characteristics for Li-Ion batteries. In addition to its exceptional puncture strength, the low-melting PE layer (135 °C) can act as a thermal fuse, while the higher-melting PP (165 °C) layers provide physical integrity. The fuse layer melts and loses porosity at elevated temperatures; the other layers do not melt and continue to provide mechanical integrity after the fuse layer has melted.

Thermal Safety

If the batteries are charged for long extensive time it gets over-heated. This will lead to breakdown of 'solid-electrolyte interface' layer, there is no reaction between anode/electrolyte, possible breakdown of electrolyte which in turn, produces large amount of heat and generates flammable hydrocarbon gases. The overcharging can be control by having battery management system externally that will take care of charging and discharging voltage and current of each cell in the pack. This will ensure the external protection of batteries over overcharging. However, there is possibility of internal voltage recharge which can be avoided by using redox shuttle additives. The overheating of the batteries can be controlled by element substitution and protective coating. Element substitution can effectively improve the thermal performance of the layered oxide materials by stabilizing the crystal structure. The protective coat is a thin layer and Li⁺ conducting compound which primarily protects cathode's surface from direct contact with an electrolyte, thereby preventing side reactions, phase transition, enhance structural stability, and reduces the disorder of cations in the crystal sites. Also, if the battery temperature rises close to the separator melting point, separator pores tend to shut down, a process known as "separator shutdown" which depends on melting point of separators. The shutdown of separators can be avoided by having triple-layered polymer separators whereas the PE layer is sandwiched between two PP layers (PP/PE/PP developed by Celgard LLC) which have already been commercialized.

Applications

Performance characteristics of NiCd, NiMH, and Li-Ion systems are summarized in Table 2 as well as in Fig. 18. Li-Ion batteries offer advantages in high energy density, high voltage, high power capability and good charge retention, and low self-discharge rate. As an advanced rechargeable battery system, Li-Ion cells can be designed in any of the typical sealed-cell constructions: coin, spirally wound cylindrical, or prismatic configurations, and have a wide range of applications. Most of the developments have concentrated on the smaller cells for portable applications. Particularly for cellular phones and laptop computers, Li-Ion batteries become predominant power sources. Large-size cells have also been aggressively developed for applications requiring high energy density and high-power capability, such as electrical vehicles (EV) and hybrid electrical vehicles (HEV).

Compared with NiCd and NiMH systems, a Li-Ion cell displays a sloping discharge curve profile. In addition, the discharge rate of a Li-Ion cell cannot be as high as that of NiCd and NiMH systems because, at high-rate discharge, diffusion steps become critical in the intercalation processes. Fig. 22 displays the diffusion coefficient (Guyomont and Tarascon, 1992) for the petroleum coke (Li_xC₆), showing that the value of the diffusion coefficient of the lithium ion in the carbon anode varies with the lithiation content at ambient temperature, which is responsible for the sloppy discharge curves. While in graphite, its diffusion coefficient is about 10⁻¹¹ cm² s⁻¹ at ambient temperature, it is about two orders of magnitude lower than the petroleum coke.

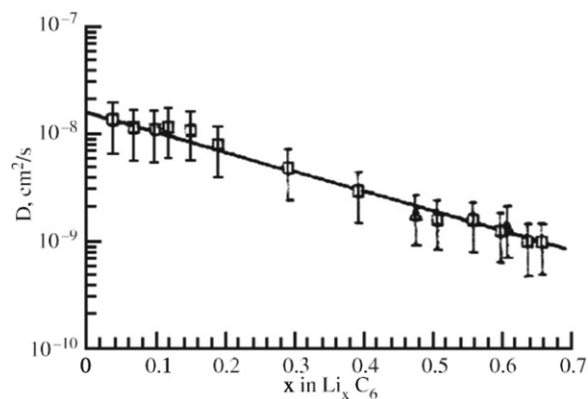


Fig. 22 Diffusion coefficient of lithium ion in petroleum coke carbon varying with lithium content (after Guyomont, D., Tarascon, J.M., 1992. Lithium metal-free rechargeable LiMn_2O_4 /carbon cells: Their understanding and optimization. *J. Electrochem. Soc.* 139, 937–941).

The graphite anode cells usually have a higher capacity at low discharge rates than the hard carbon cells, but they may lose this advantage at higher current drains. The diffusion coefficients of lithium ion (D_{Li^+}) in the lithiated metal oxides are in a range from 2×10^{-7} to $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, depending on the nature of the oxide, and also the measuring techniques. The diffusion steps play a significant role in the mechanistic aspects of the intercalation process. On the other hand, aprotic organic electrolytes must be used because of the reactivity of lithium in aqueous electrolytes, but their conductivities are poor. Therefore, these intrinsic properties may limit the high-rate capability of Li-Ion rechargeable batteries.

In high-power applications, the relatively low-rate capability during continuous discharge is a drawback. However, in addition to the intrinsic structural and chemical features of the active materials, the battery performance is also strongly affected by engineering/processing factors. It is desirable that the technical conception of the electrodes should provide maximum utilization of the reversible capacity and the high-power performance, which means the lithium intercalation/deintercalation reaction (charge/discharge reaction) allows high current densities. Thin-layer electrodes that are made from small particle-size graphite may achieve the high-rate capability of a carbon electrode. Furthermore, as the rate-limiting process is diffusion polarization, the maximum current can be very high on pulse discharges as well as on pulse charge. Therefore, the Li-Ion battery can be capable of handling the peak power requirements encountered in high-power applications such as HEV.

For high-energy and high-power applications, large-size Li-Ion cells are demanded. It has to be noted that the processing control becomes more important. A significant effect of inhomogeneous current density distribution, caused by ohmic drops along the electrode, difference in the morphology of the active materials, variations of separator properties, or the distance between the electrodes should be addressed and well controlled. Variation in current density is paralleled by variation in electrolyte concentration, which affects the potential of lithium intercalation or deposition.

For Li-Ion batteries, over discharging should be avoided as it may cause a performance problem, due to internal short-circuiting resulting from the anode current collector. It is also necessary to control the charging process. The charging voltage is a key parameter and should be limited during charging. For example, for LiCoO_2 cells, it is about 4.2 V; for LiNiO_2 cells, it is about 4.0 V. Higher charge voltages may cause decomposition of the electrolyte at the positive electrode with a rise in the internal pressure and the plating of lithium on the anode surface.

Li-Ion batteries have relatively shorter cycle life compared to NiCd and NiMH batteries. This may be attributed to structure damage resulted from lattice expansion and shrinkage as well as to the continuous lithium deposition on the anode during repetitive charge/discharge cycling. Similarly, to all other rechargeable battery systems, limiting the charge/discharge range during operation to a small window of its entire capacity will enhance the Li-Ion cell durability. Nissan commercialized HEV (Tino) was equipped with Li-Ion batteries in 2000, which indicates that Li-Ion battery technology is a promising choice for HEV applications. Proper design of the battery pack is important to assure optimum, reliable, and safe operation. It should be noted that the performance of a cell in a battery could be significantly different from that of an individual cell. The cells cannot be manufactured identically. When the cells encounter a somewhat different environment in the battery pack, the behavior of each cell may be different. During cycling, the cells in the pack can become imbalanced and have different voltages. This could result in poor performance or safety problems. Good battery technology provides opportunities to make the best use of cells.

Among the battery technologies, an important requirement is thermal control and management. The heat generated during charge and discharge, especially under high-rate operation, must be dissipated effectively to maintain the battery within a safe temperature range. To achieve this management and control, many control devices are installed in the battery pack to monitor the temperature, such as thermistor (for DT , DT/Dt control); thermostat (for TCO control); thermal fuse (for protection against thermal runaway); and positive temperature coefficient (PTC, for current as well as temperature control) device.

Recent advances in battery energy control have incorporated the use of microprocessor-based controllers within the battery to manage both the charge and discharge. Chips are designed for monitoring and controlling the battery and are being incorporated

into the battery pack, creating the so-called 'smart battery,' into the battery-using equipment, or into the battery charger. Some of the features include:

- A capacity indicator, commonly known as a 'fuel gage,' to estimate the remaining battery capacity by factoring in such variables as the discharge rate and time, temperature, self-discharge, charge rate and battery history.
- Charge control. The microprocessor can monitor the battery during charge by controlling the voltage, charge rate, and other termination parameters, such as t , DT/Dt , DV/Dt , to cut off the charge or switch to a lower charge rate; or switch from one charge method to another. The constant-current method, constant-voltage method, and pulse charging can all be controlled by the microchips.
- Discharge control, which is provided to control rate, voltage, cell equalization, and temperature management.

Furthermore, a foundation of battery normalization, modeling and control techniques (Usuda and Kayano, 1997; Wiegman and Vandenput, 1998) has been developed and presented for high-energy, high-power EV, and for high-power and charge-sustaining HEV applications. The system controls the discharge current and power output based on battery state of charge (SOC) and vehicle demand, manages cell balancing, and regulates the regeneration charge process, as well as thermal management.

The sophisticated battery modeling technology maintains energy balance by both monitoring and regulating the SOC in pre-determined limits (e.g., 0.4–0.8), in order to make the best use of the battery in terms of availability of different functions, battery life, charge and discharge efficiency, etc.

The recycling of rechargeable batteries like Ni-Cd, Ni-MH and Li-ion is essential as we can extract raw materials from used batteries and reuse it for production of other units. This process will reduce the cost of new products, protects resources and reduces pollution. Many recycling process was adopted by industries such as hydrometallurgy, pyrometallurgy, high-efficiency composite technology, electrochemical process, mechanical chemical process, physical process, and biological metallurgy process. Of this hydrometallurgy process is very simple and has high product purity with high recovery rate. The environmental impact of this process is comparatively low and widely used (Lin *et al.*, 2021).

Conclusion

The current status of rechargeable batteries, including the NiCd system, the NiMH system, and the Li-Ion system, has been reviewed. The market demand is obviously a strong driving force for the research and development of advanced energy storage technology. Scientific breakthroughs are always the pioneer to create new materials, new technology, and new rechargeable battery products.

Since 1990, the interest in electrochemical technology and rechargeable batteries, in particular heightened by the recent emphasis on battery development for portable electronics, energy storage, and electric vehicles, has resulted in significant improvements in the NiCd system, and created new technology such as NiMH and Li-Ion rechargeable batteries. These three systems are currently the major players for mobile electrical energy resources. The development of rechargeable batteries with higher energy density, higher power capability, better reliability, and lower cost to meet the market needs remains a persistent challenge.

For many practical applications, in particular for telecommunications, electric vehicles, and hybrid electric vehicles, the technology of battery management, including thermal management and energy management, has attracted great efforts and obtained great successes, both in electronic controllers and in battery modeling.

Electrochemical technology and rechargeable batteries are areas with very promising futures and technical challenges, and provide a wide range of opportunities for materials science, electrochemistry, and engineering.

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Ion Selective Membranes

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Abstract

Efficient ion sieving through artificial ion-selective membranes (ISMs) is the key parameter to extend separation technologies and improve analytical chemistry approaches. In an effort to provide a general overview of current progress in designing, manufacturing, and implantation of ISMs, this review paper gives a broad picture of the different types and various applications of ISMs. Generally, the process of selective ions transfer across the membranes relies on two dominant mechanisms of size exclusion and charge repulsion. Inspired by the natural membranes, the key players responsible for controlling ion transfer through ISMs are acceptor/ionophore components and nanopores/nanochannels. Since the early development of conventional plasticized-dependent ISMs in the mid-1960s, a wide spectrum of constituent materials, fabrication methods, and regulatory parameters have been applied to improve the selectivity and sensitivity of membranes. Taking into account these concepts, ISMs have been employed in various applications ranging from environmental and biomedical applications to manufacturing redox flow batteries and electrochemical energy storage systems.

Key Points

- Modern ion-selective membranes (ISMs) play crucial role in a wide range of applications, from biomedicine to energy conversion and storage.
- Precise ion selectivity through membranes relies on incorporating specific ionophores or generating suitable nanochannels.
- ISMs have attracted increasing attention for monitoring and removing ionic pollutants from environmental resources.
- ISMs-based systems have found an extensive application in sensing trace amounts of ions in body fluids as well drug delivery and designing wearable devices.
- The choice of suitable ISM has an extensive impact on the efficiency and sustainability of various fuel cells and batteries.

Introduction

The first generation of ion-selective membranes (ISMs) was introduced in 1937 by Izaak Kolthoff as a disc-shaped silver halide electrode (Kolthoff and Sanders, 1937). Achieving a milestone, the modern ISMs have been developed in mid-1960s by designing ion-selective electrodes (ISEs) based on a polymeric liquid membrane for measurements of calcium and fluoride ion activity with high selectivity over other anions (Frant and Ross, 1966). Later on, considerable efforts have been devoted by Pungor's research group to establish precipitate-based ion-selective electrodes and investigate their action mechanisms (Pungor and Tóth, 1973). Meanwhile, a new line of studies has been developed relying on the incorporation of neutral ion carriers in potentiometric ISEs for the detection of metal ions in biomedical applications (Oggenfuss *et al.*, 1986). Taking into account the importance of ion selectivity for various fields, a vast number of studies have explored their applications in biomedicine (for sensing gases, metabolites and electrolytes in biofluids) (Yan *et al.*, 2016), food industries, environmental analysis (Zuliani and Diamond, 2012; Crespo, 2017; De Marco *et al.*, 2007; Tang *et al.*, 2018), analytical chemistry, redox flow batteries (RFBs) (Hu *et al.*, 2021; Xiao *et al.*, 2022a), and electrochemical energy storage systems (EESs) (Park and Choi, 2022).

A classical ISE consists of a passive solid or liquid membrane which selectively allows the uptake or transport of particular target ion(s). The membrane potential could be measured under thermodynamic equilibrium at the sample-membrane interface according to the Nernst equation (Johnson and Bachas, 2003). Typically, membrane selectivity can be achieved by either incorporating specific ionophores/ion acceptors or generating suitable nanopores/nanochannels in the matrix. As the more conventional ones, ionophore-based ISMs are generally composed of (1) a plasticizer and (2) a polymeric matrix, which are doped with (3) anion/cation exchanger components and (4) ionophores/ion acceptors (Sanders *et al.*, 2017). Despite their small portion (< 1 % w/w), ionophores are defined as the key functional part of these ISMs, due to their determinative role in passing or trapping of a specific ion. Given to recent technological advancements, nanostructured-ISMs have emerged as a powerful tool revealing improved selectivity, reasonable

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size/shape flexibility, tunability, and cheaper fabrication. A wide range of solid-state or bio-inspired ion nanochannels have been constructed in 0D (porous nanomaterials), 1D, 2D, or 3D geometries. In general, an ideal ISM should present high ion conductivity, suitable stability, significant selectivity over interfering counter- and co-ions, short response time, and long lifetime.

Of note, ion-selective transport through the membranes may be affected by important parameters that should be considered when choosing, manufacturing, and using the membranes. First and foremost, the chemical composition of the nanochannels/nanopores, specially on the inner face, have a direct impact on various physical properties of the channel, such as wettability, surface charge, etc (Soozanipour *et al.*, 2021). The morphological feature of nanochannels is the other critical factor to describe ion transport through artificial and natural membranes. Generally, nanochannels having symmetric or asymmetric structures and various shapes like sphere, cylinder, and gyroid. That results in them showing distinct characteristics, such as rectification capacity and ion selectivity (Lu *et al.*, 2020; Razmjou *et al.*, 2020). In addition, the membranes' performance is strongly dependent on the dimensions of nanochannels usually having pore diameters in the range of few angstroms to hundreds of nanometers (Razmjou *et al.*, 2019a). Hence, size-selective separation methods are among the most popular strategies that rely on the precise control over ion transport via defined domain sizes. Charged surfaces induce electrical double layer (EDL) in surrounding ionic liquids, which could be roughly estimated by Debye length (λ_D) as the thickness of the double layer. The higher surface charge density of channels' internal wall results to the stronger repulsive EDL forces for co-ions. On the other hand, as the ionic strength of a solution increases, greater shielding occurs by the present counter-ions and the thickness of the EDL decreases (Ahmadi *et al.*, 2021). For nanochannels, when the core size is less than the Debye length, the double layers overlap and counter-ions pass through the nanochannels as the dominant charge (Razmjou *et al.*, 2019a).

Regarding the Eisenman theory, the anionic field strength of the binding sites is a critical element determining the selectivity of alkaline metal ions through ion-exchange materials (Eisenman, 1962). That in turn reflects the distinct hydration free energy of ions and their interaction energy with a charged binding site within the channel. This led to a sequence of $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ in high anionic field strength, whereas it is vice versa in lowest anionic field strength (Laio and Torre, 1999). Moreover, some environmental factors such as pH, operating pressure, flow velocities, feed and product concentrations, temperature fluctuations, and current density can affect ion transport and selectivity of ISMs (Sun *et al.*, 2015). Mainly, the electrical field have a significant impact on ion selectivity owing to its critical role as the driving force for ion movement towards opposite electrodes. As a general rule, ions that have the opposite charge of nanochannels are specifically conducted (Razmjou *et al.*, 2019a).

Different type of substances, manufacturing processes, and modification methods have been investigated towards the fabrication of ISMs. According to the literature, ionophore-based membranes are abundantly synthesized by drop-casting of a mixture of a components in an organic solvent, like tetrahydrofuran (THF). Some modern techniques, like 3D printing, have been recently expanded for the rapid fabrication of ionophore-based ISMs with desired sizes and complex shapes (Glasco *et al.*, 2021). On the other hand, various approaches have been employed for constructing nanochannels based on chemical self-assembly or micro/nano-fabrication procedures. Thanks to recent progress in the development of modern micromachining systems, it has become possible to produce artificial ion nanochannels as small as 1–2 nm (Soozanipour *et al.*, 2021). For example, track etching technique takes the advantage of X-ray, electrons, energetic heavy ions, or UV irradiation to form tracks in polymers, which are subsequently transferred to homogeneous nanometric pores after being exposed to an electric field or chemical etching (Tan and Rodrigue, 2019). Also, different types of lithography technology like high-energy beam lithography (Chen, 2015), interference lithography (Chen and Zhang, 2018), and nanoimprint lithography (Guo, 2007) have widely been applied for writing on the surface of the materials to create chemical/physical changes and build homogenous nanochannels. Particularly, an increasing research interest has been devoted to nanoimprint approaches due to their time- and cost-effectiveness, simplicity, and great potential to be scaled up (Oh *et al.*, 2021). However, this technique relies on specific master molds and requires high-tech equipment, which restricts its widespread application. Given the recent advances in 3D printing technology, two-photon polymerization technique (TPP) overcomes the microscale resolution limit of conventional 3D printers and can be a promising alternative for traditional methods (Geng *et al.*, 2019). Indeed, the unique structural properties of nanoporous electrospun membranes, like good mechanical strength, controllable thickness, low-density, excellent pore interconnectivity, and high gravimetric porosity, offer electrospinning as an emerging approach for the fabrication of ISMs (Kim *et al.*, 2016). Apart from the mentioned techniques, some other methods have been also frequently used for the fabrication of ISMs (e.g., hot embossing (Yin *et al.*, 2018), polymer self-assembly (Wang *et al.*, 2021), stress release processing (Huang *et al.*, 2010), PDMS deformation (Chantiwas *et al.*, 2011)).

The growing interest in ISM research is closely linked to the importance of precise ion selectivity in a wide range of applications, from biomedicine to energy conversion and storage. To provide a snapshot of the most recent innovations in this field, various aspects of ISMs are covered in this article. Despite their remarkable diversity, ISMs could be categorized into two major groups, the ion acceptor/ionophore-based ISMs and nanopore/nanochannel-based ISMs, which are in turn divided into specific subsections. Next, different applications of ISMs are comprehensively discussed, with a special focus on fuel cell and battery applications. Consequently, to understand the main risks and limitations of ISM technology for further commercial usage, some critical challenges facing ISMs application are summarized.

Types of Ion-Selective Membranes

Ion Acceptor/Ionophore-Doped ISMs

Ionophores (historically named membrane-active ligands) are originally introduced as the main player of ion transport through biological membranes. They could preferentially bind to specific ions, facilitate or hinder their passing, and consequently keep the

critical ionic charge distribution across the membrane (Doebler, 2000). Beyond the wide range of natural ionophore/ion acceptors, several synthetic components have been produced with impressive selectivity for the target ions (Amemiya *et al.*, 2000). Organic polymers, like polyvinyl chloride (PVC), are the most popular matrix components, whereas there are some reports on applying solid crystals, glasses, ceramics, and liquid polymers as the matrix of ISMs (Pechenkina and Mikhelson, 2015). The majority of ionophore-based ISMs are dependent on plasticizers, which are not only improving elasticity and mechanical properties of the membranes but also acting as solvents to provide proper dispersion of ionophores. Lipophilic ionic additives of the same charge can also be incorporated into the membranes to generate repulsive forces against counterions (Wardak, 2009).

PVC-based ISMs (plasticizer-dependent)

PVC-based ISMs have been widely used for industrial, environmental, and clinical applications due to their low cost, mechanical strength, simplicity of manufacturing, high sensitivity, and suitable selectivity. Particularly, they are applied as the main sensing component of potentiometric ion-selective electrodes (ISEs) to detect various analytes in aqueous solutions (Mohan and Kumar, 2021). The performance and lifetime of an ISM could be impacted by the composition and physiochemical properties of its components. Plasticizers are small molecules with low molecular weight that commonly have an esteric structure and contain an aromatic ring. They are commonly added to the ISMs to reduce their glass transition temperature, improve their mechanical characters, and facilitate their fabrication and handling processes. Moreover, the higher polarity (dielectric constant) of plasticizers could lead to PVC-based ISMs better selectivity over counter ions and their lower detection limit (Mihali and Vaum, 2012). The most abundant plasticizers are 1-chloronaphthalene, 2-nitrophenyl octyl ether (o-NPOE), 2-fluorophenyl2-nitrophenyl ether (FPNPE), bis(2-ethylhexyl) sebacate (DOS), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate (TEHP), and sodium tetraphenyl borate ($\text{NaTP}=\text{B}$).

However, the major concern of using conventional organic plasticizers is the gradual leaching of components (plasticizers, ionophores, or lipophilic anions) out of the membranes, which could disturb the function and limit the lifetime of the systems. Further, the inherent toxicity of the exuded materials causes severe adverse effects, such as inflammatory responses to human health and the environment (Cánovas *et al.*, 2019). To address this issue, membranes with higher lipophilicity have been developed via adding a long alkyl chain to the plasticizers/ionophores (Yin *et al.*, 2017). In another approach, ionophores have been covalently immobilized within polymeric matrix, either by grafting on nanoparticles (NPs) (Jágierszki *et al.*, 2010) or using reactive plasticizers (Bodaghi, 2020). Also in some cases, the composition of PVC-based membranes with other polymeric membranes like a secondary layer of silicon rubber was successfully implemented (Joon *et al.*, 2019). Recently, branched and hyper-branched polymeric plasticizers based on adipic acid, poly(ϵ -caprolactone), and polyglycerol have received much attention because of their bigger molecular size and more free volume in comparison to the linear compounds (Zhang *et al.*, 2021). Even with the significant advances of plasticizing techniques, PVC-based ISMs still suffer from safety and stability issues. Indeed, their poor electrochemical performance and low adhesion to electrodes limit their application as ISEs, specially in biomedical devices.

Self-plasticized polymer-based ISMs

Self-plasticizing polymeric membranes were proposed as powerful alternatives to traditional plasticizer-dependent ISMs. For most of these cases, start of polymerization process relies on a polymerization initiator like ultraviolet (UV) irradiation (Abramova and Bratov, 2022). The most abundant polymers that have been used to replace PVC matrix are polyurethane, polysiloxane (silicone rubbers), polyacrylate, polythiophene, polyaniline (PANi), and polymethacrylate. All these materials have relatively low glass transition temperature (T_g) with self-polymerization ability at room temperature. However, in general, their fabrication is rather complex and/or have revealed weaker response characteristics in comparison to the conventional plasticizer-dependent ISMs (Heng and Hall, 2000).

Silicone-based ISMs showed reduced cytotoxicity, low thrombogenesis and negligible inflammatory reactions; yet have superior adhesion capacity to a wide range of substrates (Chen and Bühlmann, 2022). As a part of solid-contact electrodes, low level of water uptake and slow diffusion of ions through the silicone matrix would be beneficial for extending the lifetime of the membrane. However, the poor solubility of some ionophores in silicone background is a challenging factor, due to the low polarity of silicone (Lindfors *et al.*, 2010). In this line, Joon *et al.* reached to a higher reproducibility of the standard potential of a K^+ -selective solid-contact ISEs via coating a conventional PVC-based membrane with a layer of pure silicon rubber (Joon *et al.*, 2019). They hypothesized that the inner layer gradually fed the outer layer regarding the usual exudation of active components from PVC structure. Despite the attractive properties of polyurethane (PU), specially for preventing non-specific protein adsorption in the medical applications, it suffers from oxidative cleavage and hydrolysis under natural condition (Ahmadi and Kim, 2020). Accordingly, polyurethane has been abundantly used in modified-forms, such as Pellethane®, KP-13, and P7281-PU, to improve the performance and antifouling property of cation- (Berrocal *et al.*, 2001) and nitrate-selective membranes (Osaki *et al.*, 2019; Yusoff *et al.*, 2019). In addition, a diverse range of polyacrylate copolymers are attracting a continuous interest in this field, regarding their facile fabrication method, remarkable selectivity, and high water-repellent property (Qin *et al.*, 2003; Liu *et al.*, 2020; Ocaña *et al.*, 2018). The polyacrylate membranes have been grafted with different ionophores/ion exchangers and revealed improved analytical parameters when used as the selective part of a sensing system (Chumbimuni-Torres *et al.*, 2006; Nurlaly *et al.*, 2021). Note that in some cases, the relatively high resistivity of polyacrylate membranes has led to unstable potentiometric responses, which needs to be rectified (e.g., by combining polyacrylate with a conducting polymer) (Rzewuska *et al.*, 2008).

Ionic liquid-based ISMs

Several studies have incorporated ionic liquids (IL) into the polymeric matrix of ISMs to improve their performance, especially for using as a part of solid-contact ISEs (SC-ISEs) (Mousavi *et al.*, 2019; Upasham *et al.*, 2021). ILs are known as organic salts founds in liquid phase below room temperature (25°C). Generally, they are composed of large and asymmetric cations and resonance

stabilized anions. Both anions and cations could be functionalized to adjust the important characters of ILs such as hydrophobicity and chemical interactions. They are nonflammable and conductive materials having very low vapor pressure and notable thermal stability over a wide range of temperatures (Noble and Gin, 2011). Local distribution of cations-anions at the interface of IL-incorporated membranes with the aqueous solution results to a stable interfacial electrical potential, leading to significant improvement in the analytical parameters (Cicmil *et al.*, 2011). In addition, some approaches applied ILs as stabilizing agents to reach to a higher signal response, shelf life, and stability (Rauf *et al.*, 2020; Amara *et al.*, 2022). However, there are serious concerns regarding the leaching of hydrophobic anion/cation compartments out of polymeric membranes combined to ILs that may interfere with the ISEs selectivity (Lindner *et al.*, 2019).

Nanopores/Nanochannels-Based ISMs

As a basic definition, the term “nanochannel” refers to a transporter with the aperture size in the nanometric scale (1–100 nm) and high length to radius ratio while “nanopores” are defined as channels having a length commensurable with the aperture size. Inspiring from the natural ion channels and ion pumps actively controlling transport across biological membranes, researchers devoted great efforts to expand the capabilities of synthetic ion transporters via mimicking important biological transport mechanisms. Recent reports have evidenced that synthetic ion channels/pores have a performance comparable to or even better than biological ones in some aspects such as current rectification and ion gating in response to various chemical/physical stimuli (Perez Sirkin *et al.*, 2020). This could be attributed to the remarkable technological advancement in the fabrication of nanostructures with desired size, shape, and charge distribution. On the other hand, reaching high efficiency and advanced selectivity over the ions having similar charge and size are the major challenges for the field going forward. Working principles, selectivity behaviors, fabrication strategies, and potential applications of nanostructured-based ISMs have been discussed extensively by Soozanipour *et al.* (2021).

Supramolecular-based ISMs

Supramolecular structures are organized entities of two or more molecules associated together as a complex system via intermolecular forces. Artificial supramolecular ion channels are simply self-assembled inside the lipid bilayer membranes from basic chemical species, with the pore sizes, dimensions, and functions similar to the natural transmembrane ion channels (Malla *et al.*, 2022). These structures have displayed good ion conductivity, while their selectivity need to be further improved. More recent synthetic supramolecular architectures have the capability for conformation switching and ion gating in response to various stimuli like voltage changes, ligand, light, and mechanical forces (Chen and Hou, 2018).

In addition, accurate control of the charge distribution on the channels’ inner wall is considered as a critical factor affecting the conductivity of ISMs. To this end, a growing body of literature highlights the importance of supramolecules for reversible modulation of surface charge and controlling the flux and nature of ion transport through the channels. Various kind of supramolecular networks have been constructed by biomolecules (Pérez-Mitta *et al.*, 2015; Shi *et al.*, 2022; Xiao *et al.*, 2022b) ions (Chen *et al.*, 2016; Gao *et al.*, 2015), polymers and foldamers (Chen *et al.*, 2010; Yan *et al.*, 2019), or complementary organic molecules (Kumar *et al.*, 2018; Cai *et al.*, 2021; Zhang *et al.*, 2016) to manipulate ion nanochannels. These structures can be formed via self-assembling process or through non-covalent interactions, like electrostatic forces, π - π interactions, and hydrogen bonding.

Carbon nanotube-based ISMs

Since the first introduction of carbon nanotubes (CNTs) in 1991, they have been widely used for selective ionic transport and flow control in nanofluidic systems. CNTs are helical microtubules of graphitic carbon with hollow cylindrical structures and 1–100 nm diameter. Over the excellent mechanical strength, unique electrical properties, high surface area, and sensible biocompatibility of CNTs, the fast fluid flow through their smooth hydrophobic core and their ion gating potential, make CNTs promising candidates for next generation ISM technology (Wu *et al.*, 2012a, 2012b).

CNT-based ISMs could effectively mimic the functionalities of biological ion channels, owing to the ultrathin pore size and the negative surface charge of the incorporated CNTs. Molecular dynamics simulations have revealed that the dehydration effect governs both the selectivity and ionic transport rate through the narrow nonpolar channels in the sub-nanometric scale (Wang *et al.*, 2018). It is evident that ions of different sizes have various hydration strength, which provides a great opportunity for tuning the selectivity of CNT-based ISMs by the adjustment of the effective internal diameter of nanotubes (Corry, 2008). While using the electrical field as a driving force causes dragging the hydration shells behind ions, the ions can be driven through the channel with hydration shells when pressure force is applied (Gao *et al.*, 2021a). In general, CNT-based membranes reveal strong cation (like H^+ , K^+ , Li^+ , and Mg^{2+})-selectivity and anion (like Cl^-) exclusion in neutral pH (Tunuguntla *et al.*, 2017; Li *et al.*, 2020). This is at least partly resulted from the high density of negatively charged oxygenated surface groups ($-COOH$, $-OH$, $-C-O-C-$, etc.) at the tip entrance of the channels (Rashed *et al.*, 2021).

However, the inherent tendency of pristine CNTs for making aggregates in aquatic solution is a limiting factor for their widespread application. So, covalent functionalization of nanotube rims with charged groups and modification of CNT sidewalls are considered as effective ways to overcome this bottleneck. These methods not only have improved the dispersion of nanotubes but also intensified ionic flow and gating capacity of the membranes (Samoylova *et al.*, 2017).

MOF/COF-based ISMs

Beyond the emerging role of metal organic frameworks (MOFs) in heterogeneous catalysis, gas storage, energy storage, and drug delivery, their application in developing ISMs have a prominent value. They are porous crystalline materials composed of metallic nodes interconnected with organic ligands. According to the wide range of building units, different construction strategies, and post-modification approaches over 20,000 structural possibilities of MOFs have been introduced so far (Furukawa *et al.*, 2013). They possess uniform angstrom-sized internal cavities with similar structures to the natural ion channels and several active sites for further chemo-, shape-, size-, and stereoselective interactions (Li *et al.*, 2021).

In a simple word, MOF membranes are constructed via bottom-up self-assembly of subunits. Different fabrication strategies could directly modulate the geometry and functionality of channels. For example, in situ growth leads to continuous MOF channels, whereas contra-diffusion method produces asymmetric MOF channels (Jia *et al.*, 2022). Moreover, to broaden their applications, in-pore surface properties of channels can be tailored via functionalization with various chemical/biological molecules. Among the big family of MOFs, MIL-121 (Ma *et al.*, 2022; Zettl *et al.*, 2021; Wei *et al.*, 2021a), MIL-53 (Ruan *et al.*, 2016), Al-TCP (Fu *et al.*, 2021), ZIF-8 (Qi *et al.*, 2022; Han *et al.*, 2022; Mohammad *et al.*, 2020), HKUST-1 (Gao *et al.*, 2021b; Wang *et al.*, 2019), and UiO-66 (Xu *et al.*, 2020a) exhibited the most efficient selective transport properties, especially for the separation of heavy metal ions. Recently, a significant interest has been devoted to designing MOF-on-MOF structures, in order to overcome some limitations in permeability, selectivity, aging, and MOF-to-substrate adhesion (Abdollahzadeh *et al.*, 2022; Xiao *et al.*, 2022c). Interestingly, by taking advantage of conductive MOFs, some ISM-free electrodes have been developed, which have displayed advanced sensing performance, higher stability, and facile fabrication in comparison to the conventional ISEs (Xu *et al.*, 2022).

Selective ion transport through the sub-nanometric MOF channels is greatly dependent on the specific interaction between the un-hydrated ions and unsaturated metal sites or functional groups on the frameworks. To reach the best performance of MOF-based ISMs, the channel charge should have the opposite sign to the targeted ions. According to the size sieving effect, the pore diameter of MOFs should be adjusted larger than the targeted ions and smaller than the interfering ions. On the other hand, different functional groups could be applied on the channels for isolating ions with similar size (Li *et al.*, 2021).

More recently, covalent organic frameworks (COFs) have received increasing interest due to their superior thermo/chemical stability, tunability and well-defined porosity (Geng *et al.*, 2020). Generally, instead of metallic nodes in the MOF structures, COFs are composed of some light elements like hydrogen, boron, carbon, nitrogen, or oxygen, which are covalently bonded to the organic linkers. However, the nanometer-sized pores (0.8–5 nm) is the main restriction factor for using COF family as the efficient ion-selective materials (Lohse and Bein, 2018). Hence, a series of MOF-COF hybrid materials have been developed with advanced selectivity and stability (Hou *et al.*, 2020; Cui *et al.*, 2021).

Nonetheless, the widespread use of MOF/COF-based ISMs for medical/industrial applications is still challenging. In particular, the long-term stability of these structures under real world conditions as well as their practicality and durability in harsh environments (like high pressure, strong electrical potential, salty solutions, and extreme acidic/basic medium) are under development. Furthermore, MOFs/COFs are considered as relatively high-cost materials with serious limitation for large-scale manufacturing (Freund *et al.*, 2021).

2D nanosheet-based ISMs

The nacre-like microstructure of two dimensional (2D) layered materials recently has attracted a great deal of attention as the next-generation of ISMs. The interstitial regions between nanosheets provide lamellar nanochannels supporting controlled passing of ions or small molecules. 2D nanomaterials are easily prepared and adjusted to the desired channel size and length by optimizing the conditions of the dispersion solution (Hao *et al.*, 2022). The ion transport behavior of these membranes can not only be affected by the operating conditions (like temperature, pH, and electric field), but can also be regulated by functionalization of their building blocks. Besides, their low thickness, high mechanical strength, and chemical stability expand the prospect of 2D materials for ion sieving application (Su *et al.*, 2022).

Graphene oxide (GO) and its derivatives are the most popular 2D materials owing to their low transport resistance, adjustable channel spacing, high adsorption capacity, and accumulation of oxygen-containing functional groups on the layers. The major mechanisms governing the ion selectivity of GO membranes rely on size sieving effect and the electrostatic interaction between ions and membrane (Abraham *et al.*, 2017). In this context, some recent reports have underscored the importance of membrane surface charge in selective ion transport, especially for monovalent ions (Zhang *et al.*, 2022, 2019). It is worth mentioning that GO nanochannels seem promising for Li^+ ion separation with high selectivity over other monovalent cations like K^+ and Na^+ (Razmjou *et al.*, 2020; Ahmadi *et al.*, 2022; Razmjou *et al.*, 2019a,b). On the other hand, MXene nanofluidic membranes provide suitable hydrophilicity and electric conductivity for selective ion transport, because of the presence of different functional groups ($-\text{Cl}$, $-\text{F}$, $-\text{OH}$, and $=\text{OH}$) on their surface and sub-nanometric interlayer spaces (Tong *et al.*, 2022; Arshadi *et al.*, 2021). Also, there is increasing interest in using composite membranes based on other types of 2D nanomaterials like black phosphorus (BP) (Yang *et al.*, 2019; Kou *et al.*, 2017), MoS_2 (Di *et al.*, 2021), graphitized carbon nitride ($\text{g-C}_3\text{N}_4$) (Wang *et al.*, 2017a), and nano-clay (Dyartanti *et al.*, 2018).

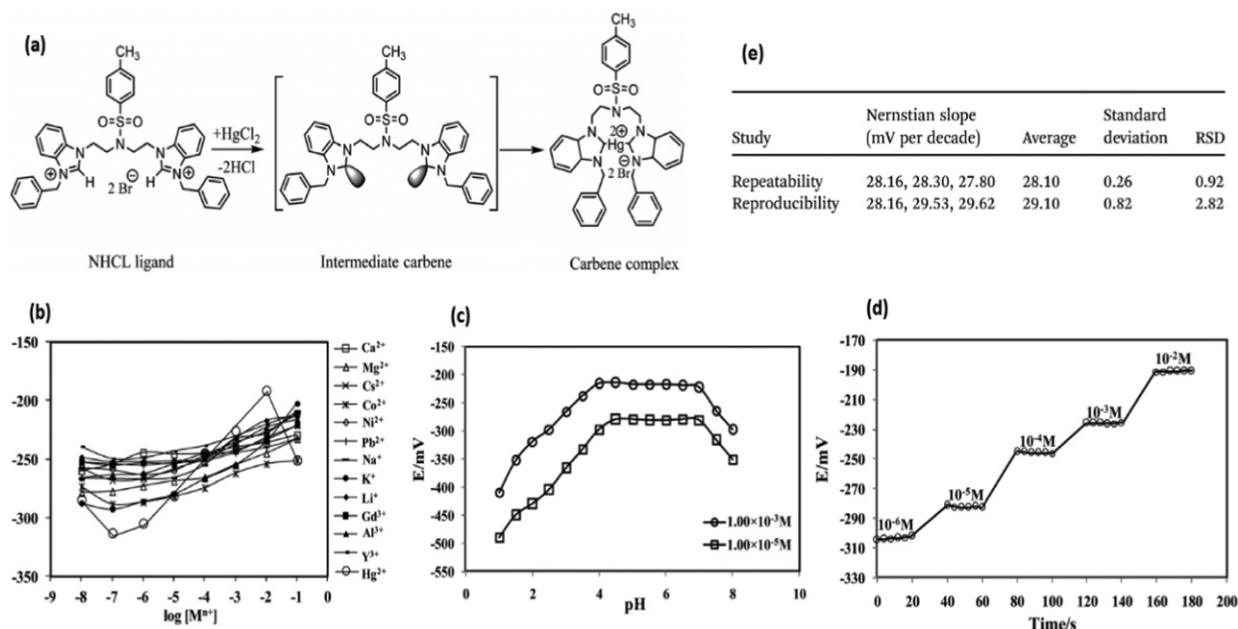


Fig. 1 (a) Schematic illustration of NHCL reaction with Hg^{2+} cation, (b) potential response of the membrane electrode to various metal cations, (c) the test solution's pH influence on the potential response of the prepared ISE, (d) dynamic response of the proposed ISE to the changes of Hg^{2+} concentration from low to high, and (e) the repeatability and reproducibility results of the membrane electrode. Reproduced with permission Said, N.R., Rezayi, M., Narimani, L., Manan, N.S.A., Alias, Y., 2015. A novel potentiometric self-plasticizing polypyrrole sensor based on a bidentate bis-NHC ligand for determination of Hg (II) cation. RSC Adv. 5 (93), 76263–76274. Copyright 2015, Royal Society of Chemistry.

Application of Ion-Selective Membranes

Environmental Applications

Water analysis

Water resources and ecosystems are being negatively affected worldwide due to human interference, making various changes in the physics and chemistry of aquatic systems (Ding *et al.*, 2021). The treatment and monitoring of water samples through precise analysis of toxic chemicals and pollutants, then removing them from the aquatic environment has a substantial effect on the quality of human life (Zielinski *et al.*, 2009; Pankratova *et al.*, 2015; Golgoli *et al.*, 2021; Chakraborty *et al.*, 2022). ISMs have attracted significant attention recently for developing potentiometric (open-circuit) sensors for environmental contaminants trace analysis due to their specific properties such as portability, fast response times, and low energy consumption. One of the important factors in the efficiency of ISMs is the proper adhesion of the membranes to their substrate which can be achieved by using a suitable matrix such as polyvinyl chloride (PVC) (Pawlak *et al.*, 2013; Pawlak and Bakker, 2014). A common matrix usually contains 33 wt% PVC, 66 wt% plasticizer, 1 wt% ionophore and some other additives with trace amounts (Kou and Liang, 2019; Zahran *et al.*, 2014). Nevertheless, using plasticizer can create some problems such as weakening the adhesion on solid substrates and leaking of the membrane matrix into the solution, resulting in the toxicity to the environment (Kisiel *et al.*, 2020). In this regard, the idea of designing and developing specific membranes without the incorporation of plasticizers using photocurable and self-plasticizing polymers has been recently developed. For instance, Jumal *et al.*, developed a photocurable self-plasticizing poly(*n*-butylacrylate) membrane using 1,2-bis-(*N*-benzoylthioureido) cyclohexane (BTCH) as an ionophore to fabricate a potentiometric sensor for the detection of Hg^{2+} metal ions. This sensor showed linear response within the concentration range of 10^{-5} to 0.1 M towards mercury ions and a low detection limit (Jumal *et al.*, 2012). Therefore, choosing the proper conducting polymer and ionophore has a great impact on the efficiency of the prepared sensor. In another research, Said *et al.*, fabricated a photocurable and self-plasticizing polypyrrole (PPy) sensor using a bidentate bis *N*-heterocyclic ligand (NHCL) as ionophore for Hg (II) detection in aqueous solutions. The proposed Hg^{2+} selective electrode showed a high efficiency in the detection of Hg^{2+} cation in the concentration range of 1×10^{-6} to $1 \times 10^{-2} \text{ M}$, with a good detection limit of $2.5 \times 10^{-7} \text{ M}$ (Fig. 1) (Said *et al.*, 2015). In a similar research, Ariri *et al.*, fabricated a Pb-ISE using acrylate-based membranes. In this way, methyl-methacrylate-co-butyl acrylate (MB28) copolymers were prepared through photo-polymerization method, then deposited on pencil graphite electrode (PGE) with a PPy-Cl thin film. The proposed membrane was plasticizer-free with a good adhesion on the electrode surface (Ariri *et al.*, 2022).

Selective removal of ions/pollutants

Selective separation of some ions such as Li^{+} , Na^{+} , Mg^{2+} , Ca^{2+} is challenging due to their relatively similar properties (e.g., size, charge and coordination number) (Lambert *et al.*, 2006; Nie *et al.*, 2017a; Warnock *et al.*, 2021; Nie *et al.*, 2017b). In this respect, a ISM can be useful as an energy-efficient, and cost-effective approach (Kazemzadeh *et al.*, 2020). However, since there are such

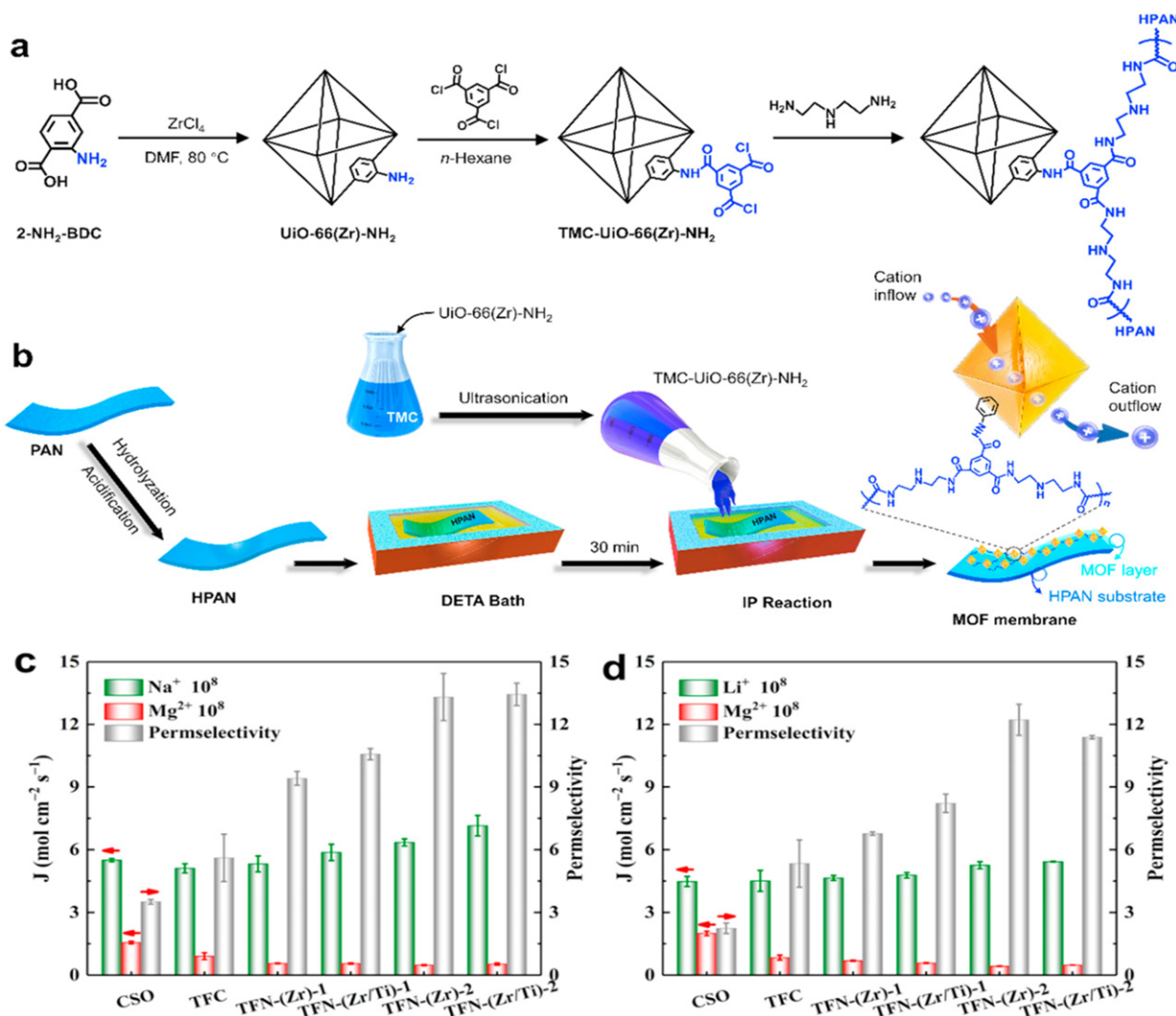


Fig. 2 (a) Schematic illustration of the preparation of polyamide-containing MOF, (b) schematic diagram for the preparation of thin-film composite membrane, and (c) ion flux (J) and, (d) permselectivity (P) of the prepared membranes in Na^+ - Mg^{2+} and Li^+ - Mg^{2+} solutions. Reproduced with permission Xu, T., Sheng, F., Wu, B., *et al.*, 2020b. Ti-exchanged UiO-66-NH₂-containing polyamide membranes with remarkable cation permselectivity. *Journal of Membrane Science* 615, 118608. Copyright 2020, Elsevier.

interferences among ions, making modifications on the surface of the membranes is highly efficient for their targeted selectivity. For instance, lithium as an energy-critical and valuable element has led the researchers to find the ways to extract Li^+ from seawater and some other resources. In this context, Zhao *et al.*, synthesized graphenes grafted with sulfonated 4,4'-diaminodiphenyl sulfone (SDDS) with a symmetrical structure (i.e., rGO-SDDS-rGO) as a cation-exchange membrane (CEM). The membrane was used for the extraction of Li^+ from Na^+ , Mg^{2+} and Ca^{2+} mixture. The prepared rGO-SDDS-rGO CEM exhibited high separation efficiency values for $\text{Li}^+/\text{Mg}^{2+}$ and $\text{Li}^+/\text{Ca}^{2+}$ at 85.32% and 80.81%, respectively (Zhao *et al.*, 2018). Graphene as a 2D material is extensively used in membrane technology due to its high flexibility, chemical stability, facile functionalization and tunable interlayer spacing (Rollings *et al.*, 2016; Qi *et al.*, 2018). However, there are some limitations in reducing the interlayer space of graphene oxide (GO) membranes and keeping this space constant during swelling. In this regard, Razmjou *et al.*, used a 2D nanofluidic vermiculite (VCT) instead of GO, to perform selective transportation of Li^+ within sub-nanometer VCT channels. VCT was chosen due to its superb thermal and chemical stability, high availability, less cost, easy exfoliation and facile scale up (Razmjou *et al.*, 2019b). VCT membranes showed a high rate of transportation for monovalent ions according to the sequence of $\text{Li}^+ \text{Na}^+ \text{K}^+$ with the selectivity ratios of 1.26, 1.59 and 1.36 for Li^+/Na^+ , Li^+/K^+ and Na^+/K^+ , respectively (Razmjou *et al.*, 2019b). Besides, as noted metal organic frameworks (MOFs) have been widely used recently in membrane separation. For instance, Xu *et al.*, immobilized UiO-66(Zr/Ti)-NH₂ on an ultrathin polyamide layer to extract Li^+ and Na^+ from seawater. The addition of Ti^{3+} ions was carried out to replace a number of Zr^{4+} , producing a negative charge within the framework of UiO-66 (Zr)-NH₂. The polyamide containing MOF showed monovalent permselectivity (P) for Na^+ and Li^+ at 13.44 and 11.38 selectivity ratios which were higher than those membranes reported in literature (Fig. 2) (Xu *et al.*, 2020b). Conversely, Chen *et al.*, used light

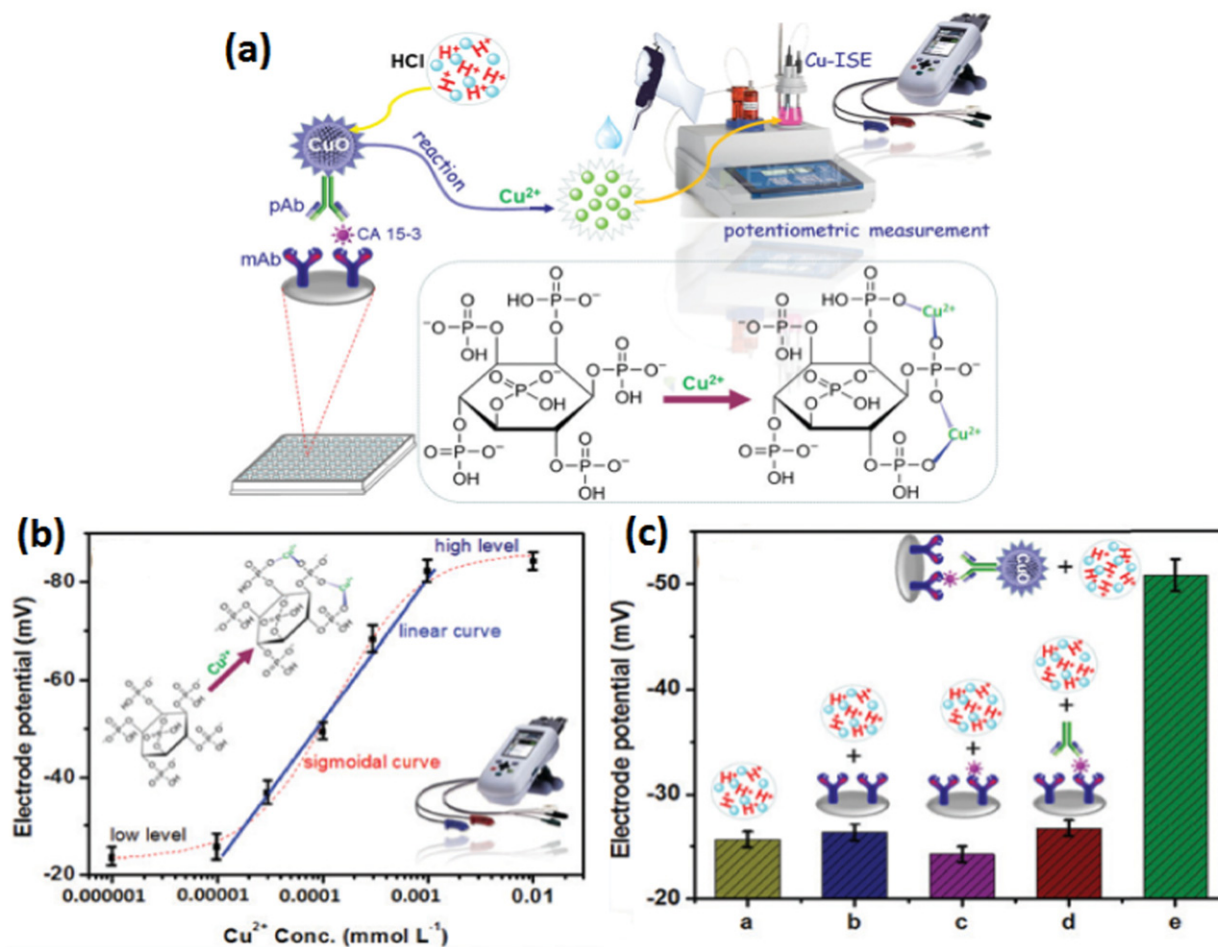


Fig. 3 (a) Illustration of the Cu-ISE-based potentiometric immunoassay for target CA 15-3 and a sandwich-type immunoreaction between Cu²⁺ and phytic acid (b) PA-GO-GDE potentiometric responses towards Cu²⁺ in a wide concentration range, (c) potentiometric responses of (a) HCl, (b) mAb + HCl, (c) CA 15-3 + mAb + HCl, (d) pAb + CA 15-3 + mAb + HCl, and (e) CuO-pAb + CA 15-3 + mAb + HCl on the PA-GO-GDE in 1.0 mM KCl solution. Reproduced with permission Zheng, M., Cao, Y.-J., Cai, W.-H., *et al.*, 2019. Phytic acid-based copper (ii) ion-selective electrode on graphene oxide for potentiometric immunoassay of breast cancer antigen 15-3. *New Journal of Chemistry* 43 (28), 11171–11177. Copyright 2019, Royal Society of Chemistry.

to control the transport and separation of Li⁺ across MOF membranes. In this work, a photochromic compound, sulfonated spiropyran (SSP), was encapsulated into the ZIF-8 crystals. SSP shows two kinds of isomers under visible light irradiation and storing in the dark, leading to an on/off Li⁺ conductivity before and after visible light irradiation (Liang *et al.*, 2020).

Biomedical Applications

Detection of biomolecules, ions, and small molecules

In addition to the application of ISMs in environmental remediation, they play a critical role in biomedical applications. Ions, whether positively- or negatively-charged, and biomolecules are omnipresent in all of the human body and effectively impact on the function of tissues and biological fluids as their concentration imbalance can induce various acute or chronic disorders (Liu *et al.*, 2019). Therefore, monitoring and sensing of such specific substances in body fluids is of great importance. Using ISMs-based electrodes for accurate monitoring of electrolytes (like Na⁺, K⁺ and Ca²⁺), pH and biomolecules (like urea, cholesterol and histidine) have been extensively increased (Karimi-Maleh *et al.*, 2021). Moein *et al.* (2015) proposed the design and development of polysulfone membrane modified with in situ imprinted sol-gel method for the detection and separation of L-Tyrosine as a lung cancer biomarker in plasma samples. They combined molecular imprinting and sol-gel methods to make a synergy between their advantages and also create a strong binding interaction between PSM and molecularly imprinted sol-gel polysulfone membrane. This membrane was coupled on-line with LC/MS/MS and showed a high extraction recovery of Tyr between 80%–85% and a reusability of up to 50 extractions (Moein *et al.*, 2015).

Since there is the high possibility of creating ion-selective sites on ion-imprinted materials, the development of ion-imprinted membranes is continuously increasing. In 2017, a Ce (III) ion-imprinted sensor was fabricated for Ce (III) detection in food. With the aim of increasing the sensitivity as well as the selectivity of the sensor, a glassy carbon electrode (GCE) was modified with a

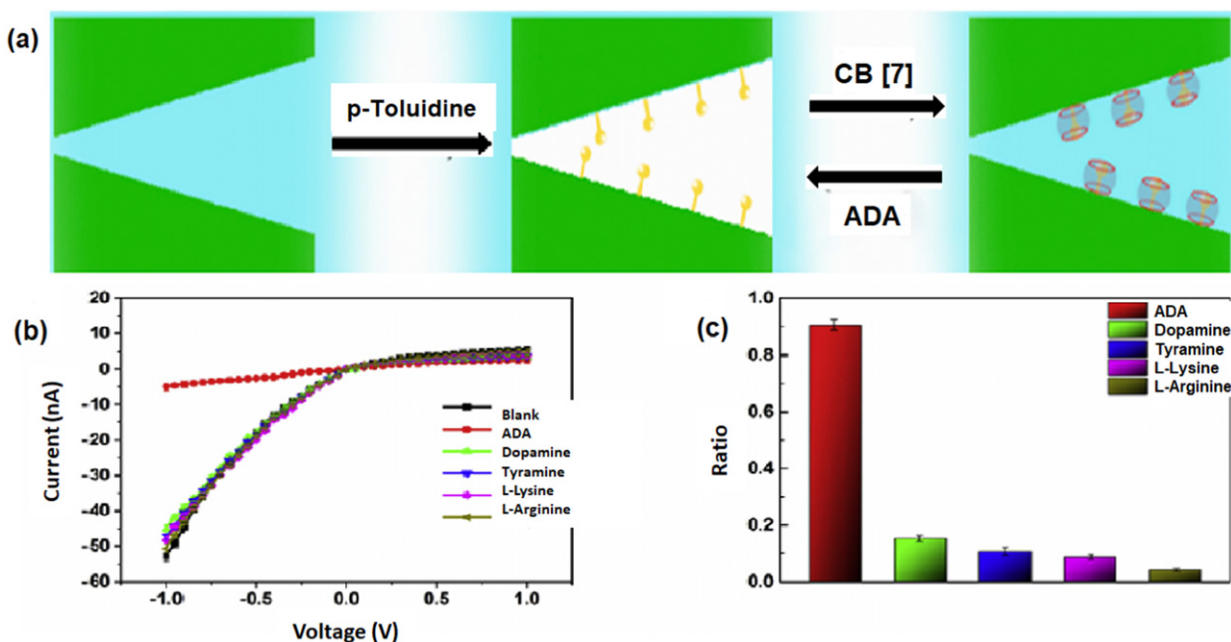


Fig. 4 (a) Schematic illustration of the host-guest mechanism of the prepared CB[7]-p-toluidine-functionalized nanochannel sensor. Selectivity of the proposed nanochannel sensor, (b) the responses of the sensor to ADA, Dopamine, Tyramine, L-Lysine and L-Arginine, and (c) the rectification ratios in the presence of five different solutions containing ADA, Dopamine, Tyramine, L-Lysine and L-Arginine. Reproduced with permission Xie, Z., Yang, M., Luo, L., *et al.*, 2020. Nanochannel sensor for sensitive and selective adamantanamine detection based on host-guest competition. *Talanta* 219, 121213. Copyright 2020, Elsevier.

poly-catechol (PC) film followed by its integration with a Ce (III) ion-imprinted membrane (IIM). The obtained Ce(III)-IIM/PC/GCE sensor revealed high capability in detecting cerium in food in concentrations ranging between 3.0×10^{-12} and 1.0×10^{-4} and the limit of detection of 1.0×10^{-12} mol/L (Chen *et al.*, 2018).

Concerning the detection of biomolecules, Santos *et al.*, designed and developed an antibody biomimetic material made of pyrrole (molecularly-imprinted polymer) as ionophore incorporated in PVC plasticized membranes to detect a protein in breast cancer antigen (i.e., carbohydrate antigen 15-3 (CA 15-3)). They prepared the plastic antibodies coupled to the potentiometric method which showed the detection limit of 1.07 U/mL with a linear response from 1.44 to 13.2 U/mL (Santos *et al.*, 2018). Zheng *et al.*, determined CA 15-3 by a copper (II) ion-selective electrode (Cu-ISE). In this work, the electric potential was obtained through the interaction between CuO-NPs labeled onto the anti-CA 15-3 polyclonal antibody as a detectable element and phytic acid immobilized on a GO-modified electrode in acidic conditions (PA-GO-GDE-based ISE). In this way, the potential of Cu-ISE was highly dependent on the composition of the target CA 15-3 in the sample and exhibited a small detection limit of 5.3 mU/mL with a vast 0.01–100 U/mL linear range (Fig. 3) (Zheng *et al.*, 2019).

Control drug release

With the development of biology and science, drug delivery systems have captured increasing attention (Li *et al.*, 2019; Wu and Yang 2017; Liu *et al.*, 2016). To improve the efficiency and reduce the toxicity of conventional medical methods, controlling drug release is greatly essential (Kamaly *et al.*, 2016; Li *et al.*, 2018). Recently, membrane-based drug delivery technologies have found an extensive application in drug delivery due to their easy usage and constant rate of drug release (Mazzeo *et al.*, 2019). Among various materials, DNA nanostructures as unique platforms are widely used to transport various biologically active components due to their customizability, permeability, biocompatibility and structural programmability (Luong *et al.*, 2018). These features lead to the usage of DNA in a variety of diagnostics methods (Zhang *et al.*, 2018; Linko *et al.*, 2015; Zhang *et al.*, 2020). Burns *et al.*, used DNA as a molecular valve with a barrel-like shape to control the transportation of cargo across a bilayer membrane. The valve consisted of seven concatenated DNA strands as pore NPs with the ability to bind a specific ligand to open up the membrane-spanning channel. The ion selectivity of NP-O was compared with a protein pore α -haemolysin (α -HL) and α -HL showed no selectivity towards cargo due to its charge-neutral lumen and pore diameter range of 1.3–2.9 nm (Burns *et al.*, 2016). In another study, Daqi *et al.* designed and prepared a nanochannel sensor based on a host-guest system to detect adamantanamine (ADA) as a veterinary drug (Xie *et al.*, 2020). In this work, the nanochannel surface was functionalized with p-toluidine followed by assembly with Cucurbit[7]uril (CB[7]). Upon the addition of ADA, it occupies the cavity of CB[7] through a host-guest mechanism, releasing CB[7] from CB[7]-p-toluidine complex and changing the hydrophobicity of the nanochannel. This strategy could recognize ADA with high sensitivity in 10–1000 nM range and detection limit of 4.54 nM (Fig. 4).

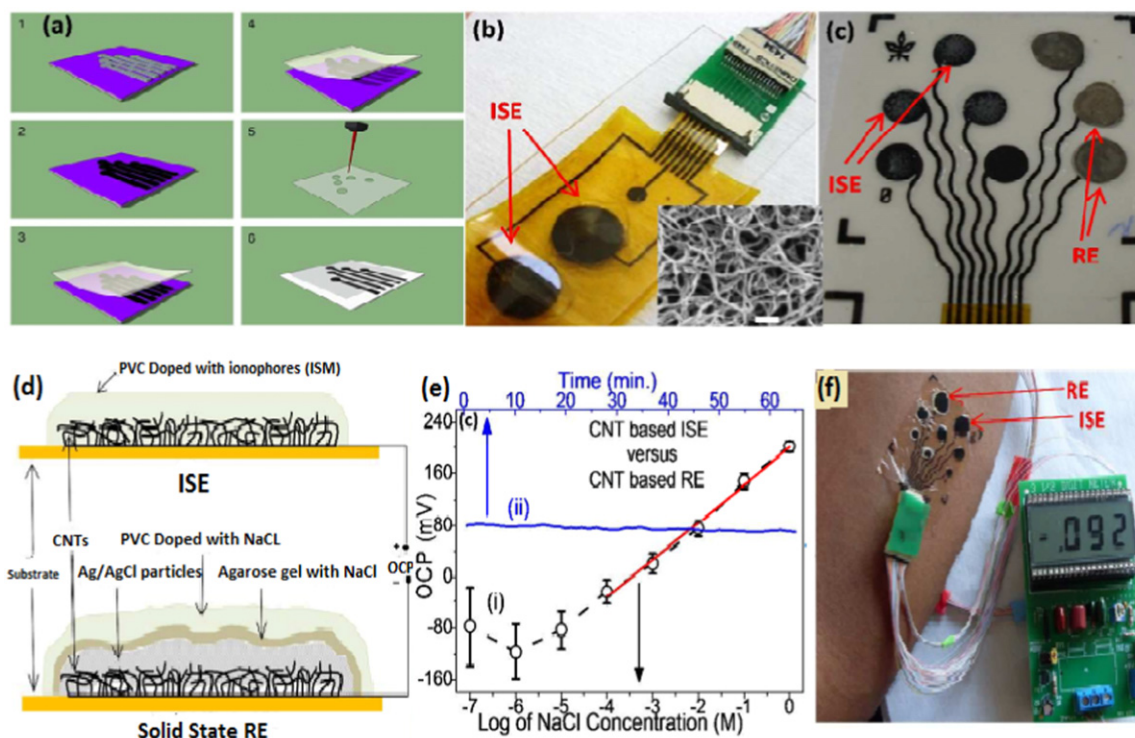


Fig. 5 (a) Schematic illustration of the fabrication of CNT electrodes, (b) ISEs on polyimide substrate. Inset is the surface scanning electron microscopy (SEM) image of the CNT electrodes, (c) CNT ISEs and REs on temporary tattoo paper, (d) schematic illustration of flexible CNT-based ISE and RE, (e) calibration of CNT-based ISE with respect to CNT-based RE (curve (i)) where curve (ii) indicates the measurement of OCP of ISE in 10^{-2} M NaCl solution versus RE for 1 h, and (f) CNT-based ISEs and REs on a flexible tattoo connected to the skin and a voltmeter. Reproduced with permission Roy, S., David-Pur, M., Hanein, Y., 2017. Carbon nanotube-based ion selective sensors for wearable applications. *ACS Applied Materials & Interfaces* 9 (40), 35169–35177. Copyright 2017, American Chemical Society.

Wearable devices

Nowadays, with the development of wearable devices, real-time electrical and chemical monitoring of various ions, biomolecules and essential biomarkers which have a critical role in human health-care, have captured much attention (Tu *et al.*, 2020; Parlak *et al.*, 2018; Nakata *et al.*, 2017). ISMs as the main diagnostic component of ion-selective electrodes (ISE) offer an opportunity to be used in wearable devices as an alternative to conventional clinical analysis methods (Liu *et al.*, 2022; Tran *et al.*, 2018). A notable challenge in conventional ISEs is their liquid part which exists between the ISM and a metal electrode (usually Ag/AgCl) and needs a container. Therefore, designing and developing solid contact ISEs have been carried out as an alternative. These small, rigid and cost-effective alternatives can couple to the skin wirelessly which is a paradigm shift in physiological monitoring (Parrilla *et al.*, 2016; Wang *et al.*, 2017b). Although they prepare estimates of some basic vital signs which is a serious challenge for vital processes, their development and commercialization is growing increasingly. For instance, carbon nanotube (CNT)-based ISEs were prepared to measure Na^+ concentration in human sweat. CNT films were used to address the poor attachment of membrane to the metal electrode. A plasticized PVC doped with sodium ionophore X and ion exchanger salt was used as ISM. ISEs showed high sensitivity within the concentration range of 10^{-4} to 1 M and the limit of detection (LOD) of 1.12×10^{-6} , while the Na^+ concentration in human sweat lies in 1–100 mM (Fig. 5) (Roy *et al.*, 2017). Despite the high conductivity of carbon nanotubes, they are unable to measure the function of air permeability on human body. In this regard, in a study, a flexible carbon nanofiber (CNF) membrane was prepared as a wearable biosensor to identify uric acid in artificial sweat. CNFs have been a focal point of interest recently resulting from their large surface area, fine diameter, inherent electrical conductivity and their cost-effective and tunable fabrication through electrospinning process (Wei *et al.*, 2021b).

In addition, recently, textile materials have gained great attention for sweat analysis due to their low cost, high sensitivity and comfort (Gualandi *et al.*, 2016). In research carried out by Coppede, a wearable textile ion-selective device was fabricated for sweat monitoring. The textile fiber was functionalized during a number of steps: first by the deposition of the conducting polymer poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and then by a ion-selective PVC-based membrane with different ionophores based on the selected ion (Coppedè *et al.*, 2020).

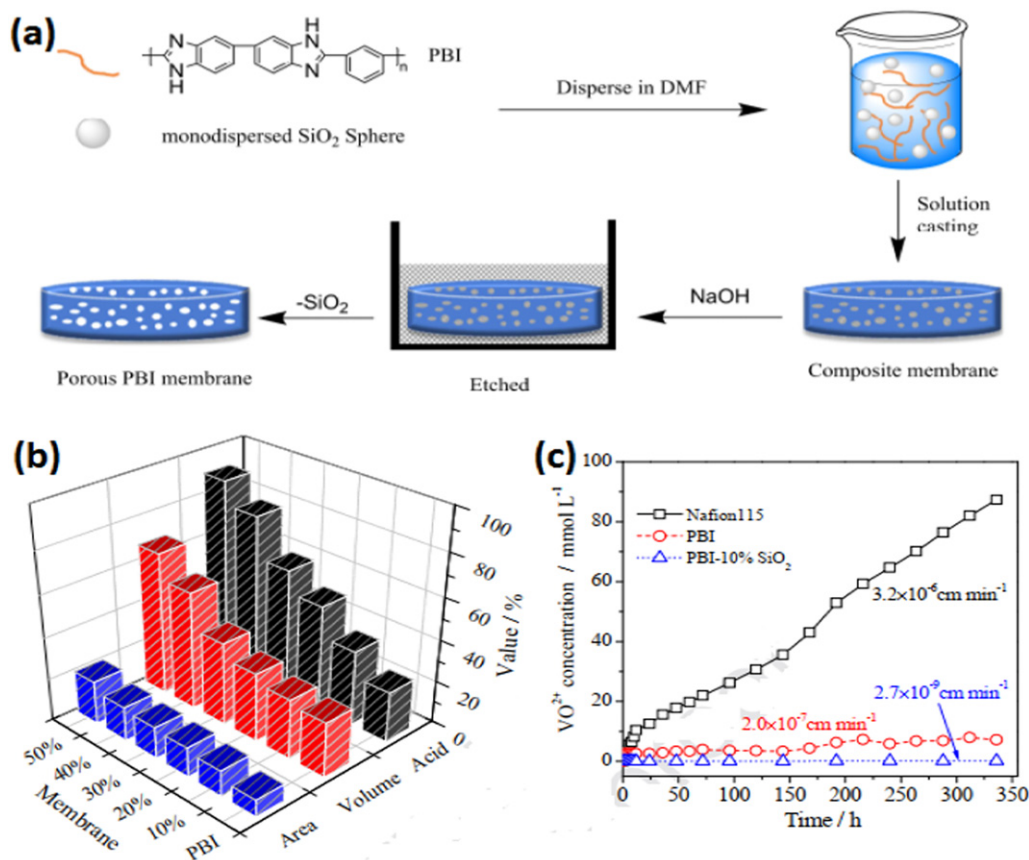


Fig. 6 (a) Schematic illustration of the porous PBI membrane fabrication, (b) Acid uptake and dimensional swellings of the prepared PBI-based membranes following their immersion into a 3 M H_2SO_4 solution, (c) Vanadium ion permeability of various PBI-based membranes compared to Nafion 115. Reproduced with permission Che, X., Zhao, H., Ren, X., *et al.*, 2020. Porous polybenzimidazole membranes with high ion selectivity for the vanadium redox flow battery. *Journal of Membrane Science* 611, 118359. Copyright 2020, Elsevier.

Fuel Cell and Battery Applications

In the past decades, due to the severe impacts of greenhouse gas emissions, a substantial need for sustainable and environmentally-benign energy resources have been increased. Among various energy conversion and storage systems, fuel cells and batteries are being developed increasingly owing to their merits such as low carbon emission, high efficiency, and flexible operations. The choice of suitable ISM as the important part of batteries and fuel cells, has a substantial effect on their efficiency (Amiri *et al.*, 2021). For instance, since nafion membranes are costly and lead to the high vanadium ion permeability in vanadium redox flow batteries (VRFB), Ling *et al.*, employed the porous composite of polyvinylidene fluoride (PVDF)/sulfonic silica as membrane. This membrane showed lower vanadium ion permeability ($1.12 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) and three times higher ion selectivity than nafion (Ling *et al.*, 2019). Similarly, Jung *et al.*, used PVDF membrane with some modifications in VRFBs. They used blend membranes comprising PVDF with low vanadium permeability, sulfonated poly (ether ether keton) (sPEEK) with high proton conductivity and urethane acrylate non-ionomer (UAN) which makes the blend membrane miscible. The addition of UAN (1–2 wt%) to the sPEEK/PVDF blend, increases the selectivity towards proton against vanadium (Jung *et al.*, 2018). In another investigation, Che *et al.*, used polybenzimidazole (PBI) membrane in VRFBs. However, due to the low uptake of sulfuric acid by PBI membrane, leading to the low proton conductivity, they made the membrane porous by adding silica particles as templates. Therefore, the proposed porous PBI membrane illustrated an extremely vanadium ion permeability ($< 10^{-9} \text{ cm}^2 \text{ min}^{-1}$) in the vanadium flow battery (Fig. 6) (Che *et al.*, 2020).

Conclusion

Ion selectivity is a significant issue in various fields, as a result of which many kinds of research have been conducted to optimize it by considering different criteria such as chemical and morphological features of nanochannels, dimensions, surface charge, binding sites, environmental factors, suitable substances, and methods, to meet the increasing demand for ion separation. Recently, nanostructured ISMs have been introduced as efficient platforms for ion separation due to their appropriate features and cost-effective fabrication. This study provides a holistic overview of the recent literature on the advanced materials and structures used for ISMs and their key applications.

Overall, there are two main types of ion-selective membranes including ionophore-based and nanochannels-based ISMs. The drop-casting and 3D printing are two advantageous methods for constructing favorable ionophore-based ISMs. PVC is one of the most popular organic polymers for fabricating ionophore-based ISMs and ISEs. Polyurethane and polyacrylate are alternatives that have substituted PVC in some previous works. In addition, some approaches have been used to fabricate nanochannel-based ISMs such as track etching and lithography, which lead to homogeneous pores construction. Creating efficient nanochannels capable to separate ions with similar charges and dimensions is critical. It is noteworthy that among various types of ISMs, 2D nanosheet-based ISMs especially GO and MXene are the most promising types for effective ion separation due to their unique properties.

Ion-selective membranes are widely used in various areas such as water monitoring and purification as well as the selective separation of pollutants and valuable ions such as Li^+ . Besides, there are some biomedical applications for ISMs some of which include: monitoring of electrolytes and body fluids, assessing foods, detecting diseases, controlling drug release (by using DNA nanostructures), and analyzing human health via wearable biosensors. Ultimately, ISMs are used as an important part of batteries and fuel cells which are eco-friendly energy resources. The high potential of ISMs to be used in varied application and their promise to make the next generation of green technologies and healthcare tools is a great motivator for studies on harnessing the power of recent advanced functional materials to develop more efficient ISMs for real-word applications.

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Advanced Energy Materials Characterization: In Situ/Operando Techniques

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Abstract

In situ/operando characterization techniques are widely used for studying dynamic processes and electrochemical, thermal, and mechanical properties of energy storage materials. It has become an essential tool to provide fundamental understanding of the material properties, reaction kinetics, and failure mechanisms, contributing to the advancement of the energy storage technologies. In this review, variety of *in situ/operando* techniques are compiled, and the experimental setups, attainable information, and limitations/requirements are explained in detail by introducing representative studies using the techniques. Finally, challenges and future opportunities for the development of the advanced *in situ/operando* characterization techniques are discussed.

Nomenclature

AFM Atomic force microscopy
ASSB All-solid-state battery
ASSLB All-solid-state lithium battery
BF-STEM Bright-field scanning transmission electron microscopy
CV Cyclic voltammetry
DEC Diethyl carbonate
DMC Dimethyl carbonate
DPC Differential phase contrast
EC Ethylene carbonate
EDS Energy-dispersive X-ray spectroscopy
EFTEM Energy-filtered transmission electron microscopy
ESEM Environmental scanning electron microscopy
ETEM Environmental transmission electron microscopy
FFT Fast Fourier transformation
FIB Focused ion beam
GLC Graphene-based liquid cell
HAADF High-angle annular dark-field
HOPG Highly oriented pyrolytic graphite
IL Ionic liquid
LAB Lithium air battery
LCO Lithium cobalt oxide, LiCoO_2
LFPO Lithium iron phosphate, LiFePO_4
LIB Lithium-ion battery
LIPON Lithium phosphorus oxynitride, $\text{Li}_x\text{PO}_y\text{N}_z$
LiPS Lithium polysulfide
LLZO Lithium lanthanum zirconium oxide
LNO Lithium nickel oxide, LiNiO_2
LPS Li_3PS_4
LPSCI $\text{Li}_6\text{PS}_5\text{Cl}$
LSB Lithium-sulfur battery
MEMS Microelectromechanical system
NMC Lithium nickel manganese cobalt oxide, $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$
NMR Nuclear magnetic resonance
OER Oxygen evolution reaction
OM Optical microscopy
ORR Oxygen reduction reaction
PC Propylene carbonate
PS Polysulfide
RF Radio frequency
SEI Solid electrolyte interface
SEM Scanning electron microscopy
SE Solid electrolyte

STEM Scanning transmission electron microscopy
TEM Transmission electron microscopy
UHV Ultra high vacuum
XANES X-ray absorption near edge structure
XAFS X-ray adsorption fine structure
XAS X-ray absorption Spectroscopy
XCT X-ray computed tomography
XRD X-ray diffraction
XPD X-ray powder diffraction
XPS X-ray photoelectron spectroscopy

Key Points

- Variety of In Situ/*Operando* characterization techniques for energy materials research are compiled.
- Capabilities and limitations of each technique are explained by introducing representative studies.
- Roles of in situ/*operando* characterizations on the advancement of energy storage technologies are illustrated.
- Current state of the art and future perspectives of advanced in situ/*operando* techniques are discussed.

Introduction

Growing awareness on climate change, environmental pollutions, and sustainability has been stimulating the global movement for a transition from fossil fuels to renewable energy sources such as solar, hydro, wind, and geothermal powers. To make this transition possible, it is of utmost importance to develop a technology that can store the generated energy and extract it when needed in an efficient and economical manner. Electrochemical energy storage devices such as battery, fuel cells, and supercapacitors have been extensively studied for the application. During the operation of these devices, significant changes to the structures and elemental distributions (reversible and permanent) can be introduced to the materials that affect the performance of the system. For example, in batteries, ions transport between the anode and the cathode through the electrolyte and reacts with the active materials by intercalation, alloying or conversion mechanisms. These reactions can introduce significant change in the crystal structure and volume of the electrode materials. The change in the chemical composition can affect the ion mobility and the stability of the structures. The large volume changes of the electrode materials in charge/discharge process can introduce stress and cause durability issues. Solid electrolyte interface (SEI) layer formed at the electrode surface reacting with the electrolyte effectively passivates the surface and prevents further decomposition of the electrolyte. Understanding the relationships between the structural and the properties of the materials and its evolution in the electrochemical process is essential for developing new materials and/or engineering processes to improve the energy storage technologies.

Many analytical techniques (X-ray/neutron diffraction, electron/optical microscopy, X-ray adsorption spectroscopy, etc.) have been used to study the structure and properties of the energy materials. Conventional ex-situ or post-mortem analyses using these methods provide useful information on the structure and chemistry of the materials. However, information obtained from these experiments does not always capture the dynamic processes occurring in the electrochemical system. Recently, more advanced in situ/*operando* characterization techniques have been developed, playing a key role in linking the structural/chemical evolution of the energy materials in the dynamic processes with the electrochemical performances.

Understanding the fundamental reaction mechanisms is essential to overcome the challenges and further develop the energy storage technologies. Electrochemical reaction is a dynamic process involving change in the material chemistry and structure. Direct observation of the phenomena in real time provides rich information about the process to promote in-depth understanding of the mechanisms. Many analytical techniques for evaluating structure and chemistry of materials can be performed in situ/*operando* under electrochemical testing environment. In addition, external stimuli such as thermal and mechanical can be applied to elucidate their effect on the structural evolution and the electrochemical performance. This article focuses on reviewing advanced in situ/*operando* analytical techniques to study energy materials and introduces some of the representative examples of the applications.

An overview of this article is schematically illustrated in [Fig. 1](#). Atomic/crystal structure of the materials can be analysed using X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the morphologies can be observed using scanning electron microscopy (SEM) and optical microscopy (OM). For the chemistry, energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) are used in combination with electron microscopy, and the chemical states can be identified using XPS and XAS.

In the following sections, detailed procedures and examples are presented to show how these analytical techniques are used in situ/*operando* to study the fundamental properties of the materials and contribute to the development of the energy storage technologies.

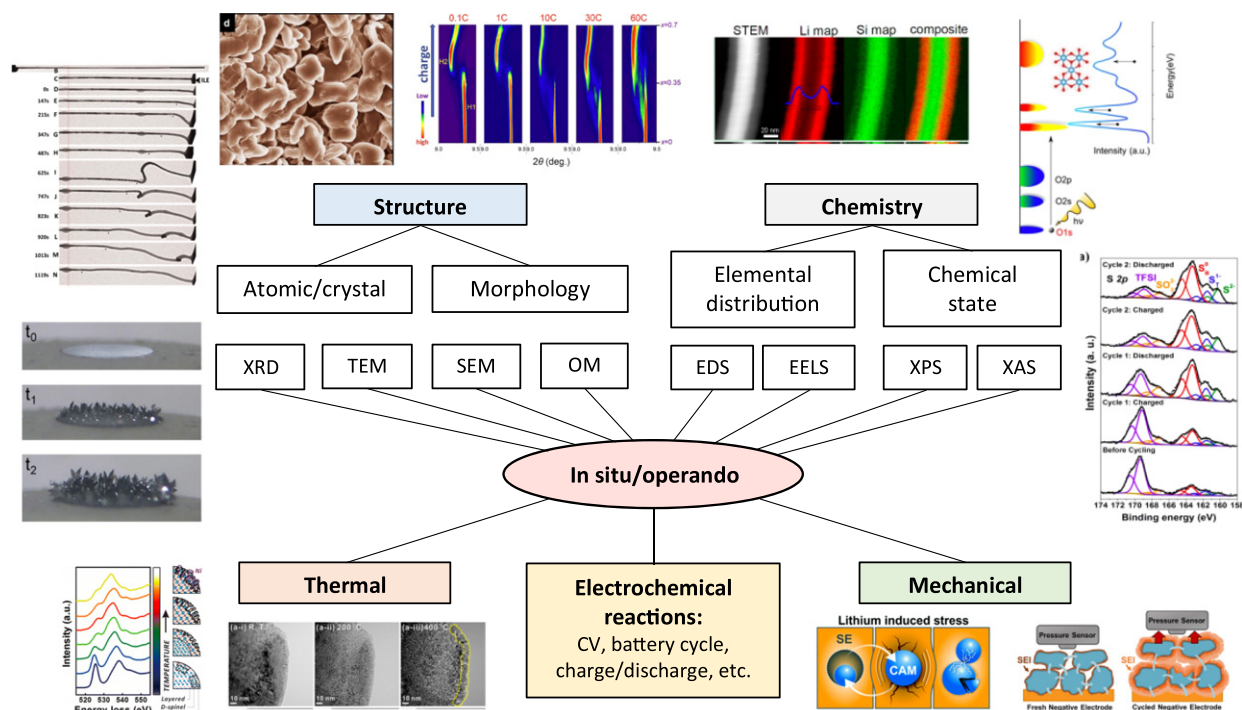


Fig. 1 Overview of the review. Images adapted or reproduced with permission from Louli, A.J., Ellis, L.D., Dahn, J.R., 2019. Operando Pressure Measurements Reveal Solid Electrolyte Interphase Growth to Rank Li-Ion Cell Performance. *Joule* 3 (3), 745–761. Available at: <https://doi.org/10.1016/j.joule.2018.12.009>. Copyright (2019), with permission from Elsevier. Koerver, R., *et al.*, 2018. Chemo-mechanical expansion of lithium electrode materials – On the route to mechanically optimized all-solid-state batteries. *Energy & Environmental Science* 11 (8), 2142–2158. Available at: <https://doi.org/10.1039/C8EE00907D>. Copyright 2018, Royal Society of Chemistry. Hwang, S., *et al.*, 2014. Investigating local degradation and thermal stability of charged nickel-based cathode materials through real-time electron microscopy. *ACS Applied Materials & Interfaces* 6 (17), 15140–15147. Available at: <https://doi.org/10.1021/am503278f>. Copyright 2014 American Chemical Society. Banik, S.J., Akolkar, R., 2015. Suppressing dendritic growth during alkaline zinc electrodeposition using polyethylenimine additive. *Electrochimica Acta* 179, 475–481. Available at: <https://doi.org/10.1016/j.electacta.2014.12.100>. Copyright 2015, Elsevier Ltd. Huang, J.Y., *et al.*, 2010. In Situ observation of the electrochemical lithiation of a single SnO₂ nanowire electrode. *Science* 330, 1515–1520. Available at: <https://doi.org/10.1126/science.1195628>. Reprinted with permission from AAAS. Qian, J., *et al.*, 2015. High rate and stable cycling of lithium metal anode. *Nature Communications* 6, 6362. Available at: <https://doi.org/10.1038/ncomms7362>. With CC-BY. Zhou, Y.-N., *et al.*, 2016. High-rate charging induced intermediate phases and structural changes of layer-structured cathode for lithium-ion batteries. *Advanced Energy Materials* 6 (21), 1600597. Available at: <https://doi.org/10.1002/aenm.201600597>. Copyright 2016, WILEY-VCH. Wang, Z., *et al.*, 2013b. Electron-rich driven electrochemical solid-state amorphization in Li–Si alloys. *Nano Letters* 13 (9), 4511–4516. Available at: <https://doi.org/10.1021/nl402429a>. Copyright (2013) American Chemical Society. Nandasiri, M.I., *et al.*, 2017. In Situ chemical imaging of solid-electrolyte interphase layer evolution in Li–S batteries. *Chemistry of Materials* 29 (11), 4728–4737. Available at: <https://doi.org/10.1021/acs.chemmater.7b00374>. Copyright 2017 American Chemical Society. Frati, F., Hunault, M.O.J.Y., de Groot, F.M.F., 2020. Oxygen K-edge X-ray absorption spectra. *Chemical Reviews* 120 (9), 4056–4110. Available at: <https://doi.org/10.1021/acs.chemrev.9b00439>. With CC-BY-NC-ND.

Background: Developing Next Generation Energy Storage Technologies

Lithium ion batteries (LIBs) have been widely accepted as energy storage devices for many applications from portable electronics to electric vehicles and grid storages (Aurbach *et al.*, 2002; Whittingham, 2012). The currently commercialized LIB uses “rocking-chair” mechanism where Li ions are inserted into or extracted from the stable frames of the host electrode materials (Nishi, 1998). A typical combination of the electrodes is graphite (anode) and LiCoO₂ (cathode) with 3.7 V cell voltage. The anode can be potentially replaced by high capacity Si or Li metal with over x10 the capacity of graphite (Chan *et al.*, 2008). A major challenge is the large volume changes in the charge/discharge process that leads to the fracture of the active materials and the loss of electrical conduction path. Significant improvement was achieved by utilizing nanostructures. Nanowires (Chan *et al.*, 2008), self-assembled nanostructures (Magasinski *et al.*, 2010), and nanotubes (Park *et al.*, 2009) were used to enhance the specific capacity and the cycle lifetime by accommodating the large volume changes. The constant change of volume also causes the solid electrolyte interface (SEI) layer formed on the electrode materials to fracture and expose the fresh surface and continuously destroy the electrolyte. The current generation of the nanostructured electrodes uses active materials covered by the stable materials to prevent the electrolyte consumption and achieved significant improvement in the cycle performance (Liu *et al.*, 2012a; Liu *et al.*, 2014; Li *et al.*, 2015).

Recently, Li metal with a high theoretical specific capacity of ~3800 mAh/g and the lowest electrochemical potential of –3.04 V versus standard hydrogen electrode is attracting attention as an anode. It has been extensively studied in past decades (Aurbach and Cohen, 1996; Aurbach *et al.*, 2002; Whittingham, 2012; Xu *et al.*, 2014) after the first lithium metal battery was

proposed in 1970s (Whittingham, 1976). Despite its promising electrochemical performance, rechargeable lithium metal battery has not been commercialized successfully to date (Li *et al.*, 2014a) in contrast with LIBs dominating the energy storage technology race. Lithium deposition/dissolution is an inherent process in the Li metal secondary battery (Monroe and Newman, 2003; Li *et al.*, 2014a). During the deposition, Li metal anode is prone to forming extended protrusions, conventionally called dendrites, causing serious problems that cause not only drastic loss of reversible capacity, but also penetration of the separator and short-circuiting, leading to catastrophic fire and even explosion of the battery (Goodenough and Kim, 2010). Numerous researches have been performed to understand the dendrite formation/growth mechanisms, and the solutions to suppress the dendrite were proposed (Naoui *et al.*, 1999; Aurbach *et al.*, 2002; Mogi *et al.*, 2002; Ota *et al.*, 2004; Zhamu *et al.*, 2012; Ding *et al.*, 2013; Zheng *et al.*, 2014).

On the cathode side, LiCoO₂ (LCO) is a commonly used cathode material in LIBs since its first successful commercially application in 1980 (Mizushima *et al.*, 1980). It has an excellent intercalation nature, high voltage, low self-discharge, little volume changes, and long cycle lifetime. However, various risks have been recognized regarding its supply-demand balance (Alves Dias *et al.*, 2018) because of its near-monopolistic supply structure (U.S. Geological Survey, 2019). If the demand for LIBs continues to increase at current rate, the Co demand will exceed its supplies in the near future (Haji and Slocum, 2019; Reuter *et al.*, 2014). In addition, LCO has lower thermal stability compared to other cathode materials (Dahn *et al.*, 1994), causing the exothermic oxygen release under heating that leads to explosion. New cathode materials to overcome these issues are being developed (Etacheri *et al.*, 2011). LiNiO₂ (LNO)-based cathode materials have been extensively studied (Kalyani and Kalaiselvi, 2005; Chen *et al.*, 2004). Amongst various candidates, lithium nickel manganese cobalt oxide (LiNi_xMn_yCo_zO₂, NMC) has become one of the most promising cathode materials (Andre *et al.*, 2015). NMCs with various Ni:Mn:Co ratios have been studied in the past two decades (Lee *et al.*, 2007; He *et al.*, 2012; Noh *et al.*, 2013). Ni-rich NMCs with less Co/Mn concentrations allow larger specific capacities, but decreased capacity retention rate and thermal stability. The rapid drop in the stability is seen as the Co content decreases (Noh *et al.*, 2013). A new cathode material completely eliminating the use of Co is recently being developed (Muralidharan *et al.*, 2020).

Technologies beyond current LIBs are also being developed. Lithium sulfur battery (LSB) is one of the promising candidates as a next generation energy storage device due to its high theoretical capacity (1675 mAh/g) with an energy density ten times greater than that of traditional LIBs (2500 Wh/kg) (Yang *et al.*, 2013). Additionally, sulfur is a nontoxic byproduct of the crude oil refining process (Zhang *et al.*, 2014; Park *et al.*, 2018) resulting in a low cost, environmentally friendly, and earth abundant element (Manthiram *et al.*, 2013; Shaibani *et al.*, 2016), which makes it a suitable selection for batteries. However, there are several challenges (Manthiram *et al.*, 2013). The poor electrical conductivity of sulfur and its discharge products (Li₂S) causes the inefficient utilization of sulfur (Evers and Nazar, 2013). The large volume expansion of sulfur during lithiation leads to the premature capacity degradation from the cracking and the loss of the active materials (Yang *et al.*, 2013). In addition, the dissolution of intermediate lithium polysulfides formed in the lithiation process dissolves into the liquid electrolyte and diffuses to the lithium anode and cause parasitic reactions leading to the dendrite growth. This so called “shuttle effect” causes low coulombic efficiency, loss of active material and premature capacity decay (Ji and Nazar, 2010; Barchasz *et al.*, 2012; Nelson *et al.*, 2012; Wang *et al.*, 2013a; Evers and Nazar, 2013). Many potential solutions were proposed to mitigate these issues by creating polysulfide entrapment to prevent the shuttle effect (Elazari *et al.*, 2011; Jayaprakash *et al.*, 2011; Wang *et al.*, 2011; Xiao *et al.*, 2012; Wei Seh *et al.*, 2013; Seh *et al.*, 2014), and modifying and optimizing the separator/electrolyte to block the polysulfide from shuttling (Su and Manthiram, 2012; Tao *et al.*, 2017; Xu *et al.*, 2017; Pei *et al.*, 2018).

The Li-air battery (LAB) has exceptionally high specific capacity (Zheng *et al.*, 2008; Girishkumar *et al.*, 2010; Scrosati and Garche, 2010) standing out from the other candidates (Van Noorden, 2014). However, there are numerous technical challenges that need to be overcome (Girishkumar *et al.*, 2010). These include low energy efficiency (Débart *et al.*, 2007; Débart *et al.*, 2008; Lu *et al.*, 2010), low rate performance (Read, 2002; Zhang *et al.*, 2010b; Zhang *et al.*, 2010a), and poor cyclability (Débart *et al.*, 2008; Cheng and Scott, 2010; Bruce *et al.*, 2012). Most LAB technologies use non-aqueous electrolyte, and the major problem is the quality of the oxygen. Non-aqueous system is particularly sensitive to the CO₂ and H₂O contamination. While it is possible to use highly purified oxygen stored in a tank, it significantly reduces the specific capacity of the LAB system as a whole. An estimate shows the LAB with O₂ tank has lower energy density than advanced LIBs (Christensen *et al.*, 2011). And the low charge/discharge rate due to inherent slow kinetics of Li₂O₂ (main reaction product in LAB) formation.

All-solid-state batteries using solid electrolyte (SE) is attracting attention because SE with much high modulus than lithium metal prevents the penetration of the dendrites and allow the use of a high capacity lithium metal anode without safety issues (Janek and Zeier, 2016; Kerman *et al.*, 2017). However, several challenges remain to be solved: (1) Penetrations of lithium through SE have been reported (Sudo *et al.*, 2014; Suzuki *et al.*, 2015; Sharafi *et al.*, 2016; Aguesse *et al.*, 2017; Basappa *et al.*, 2017) with grain boundaries and pre-existing defects proposed as possible causes; (2) slow Li diffusion at the Li/SE interface (Wenzel *et al.*, 2015; Wenzel *et al.*, 2016; Richards *et al.*, 2016; Zhu *et al.*, 2016) and its nano-scale structural change when in contact with Li further reduces the conductivity (Ma *et al.*, 2016); and (3) A high compressive stress imposed on SE due to the large volume change of the lithium electrode (Wainwright and Shimizu, 1991). If these issues are to be solved, all-solid-state batteries with specific energy over 400 Wh/kg and energy density beyond 1000 Wh/L can be achieved (Randau *et al.*, 2020).

In summary, significant efforts have been paid to develop various energy storage technologies identifying the issues and finding the solutions. Many of the challenges requires understanding of the changes in the chemistry and structure of the materials associated with the electrochemical reactions occurring under the device operations. There are tremendous opportunities for the advanced characterization techniques for studying the fundamental structure and properties of the materials and associating their dynamic evolutions with the electrochemical reactions. In the following sections, applications and future opportunities of advanced in situ/operando characterization techniques are discussed.

In Situ/Operando Electron Microscopy

Open-Cell TEM

Since the first introduction of an in situ TEM technique to directly observe lithiation process of SnO_2 nanowires (Huang *et al.*, 2010), the technique has been widely used to analyse the electrochemical reactions in nano-/atomic-scale to understand the fundamental reaction mechanisms contributing to the development of energy storage materials (Wang *et al.*, 2010; Kushima *et al.*, 2011; Liu and Huang, 2011; Liu *et al.*, 2011a,b,c; White *et al.*, 2012; Li *et al.*, 2014b; Basak *et al.*, 2022). At the early stages of the development, the applications of the technique were limited by its high vacuum condition inside the TEM column because the materials were exposed to the TEM environment (*open-cell*). There were two main strategies to overcome this issue and observe the electrochemical reactions as shown in Fig. 2(A), and the experiments are performed using a special TEM holder with a piezo manipulator and biasing capability. The key difference is a type of electrolyte used for the experiment, liquid or solid.

Due to the high vacuum inside electron microscope, the electrolytes used in actual batteries (Xu, 2014; Li *et al.*, 2016; Quartarone and Mustarelli, 2020; Fan and Wang, 2021) cannot be used because these liquid electrolytes evaporate inside TEM column. Here, ionic liquid (IL) solvent with low vapor pressure is used to prevent its evaporation inside TEM allowing electrochemical reactions (Huang *et al.*, 2010). Direct observations of the reactions in real time at nano-/atomic-scales provide rich information of the dynamic processes of the electrochemical reactions which cannot be captured by traditional post-mortem analyses. Since the electrolyte wets the materials and blocks the electron beam if the liquid layer becomes too thick, 1D or nanowire geometry of the sample is ideal for this set up. The tip of the nanowire is immersed in the IL electrolyte and the electrochemical reactions can be observed at the area away from the electrolyte. Active materials can be simply brought to contact with the naturally grown oxide on a lithium metal (Liu *et al.*, 2011c; Lee *et al.*, 2016). The oxide layer is formed from a short exposure to air when the holder is transferred from a glovebox to TEM, which acts as a solid electrolyte.

The open-cell configuration relies on the use of IL or solid electrolytes which creates different environment compared to the conventional batteries using liquid electrolytes. However, it gives important insights towards understanding the atomic-scale mechanisms in the electrochemical reaction. For example, core-shell reaction morphologies were observed in a fast lithiation of

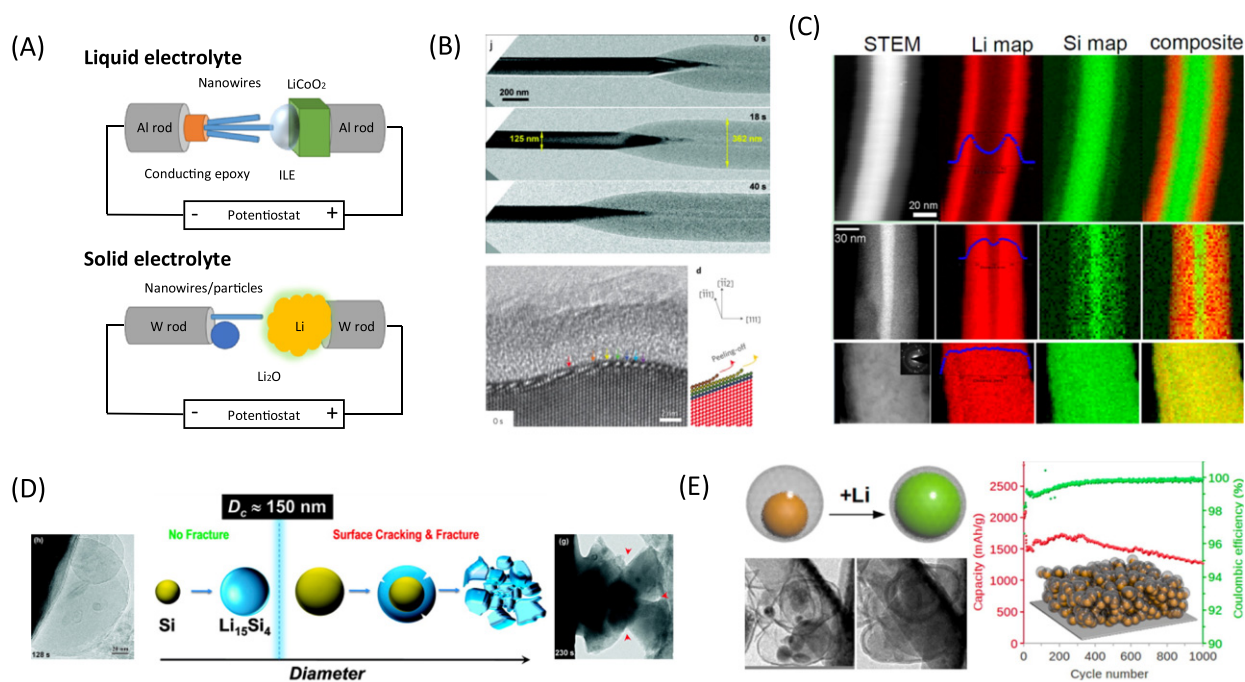


Fig. 2 (A) Typical in situ TEM configuration for open-cell setup. (B) Lithiation of Si nanowire captured by in situ TEM. Core-shell reaction propagates from outer surface inward the core in a layer-by-layer reaction. (C) STEM EELS elemental mapping of the reacted Si nanowire. (D) Size dependency of the mechanical fracture of Si nanoparticles. (E) Yolk-shell structure confines Si nanoparticles inside a C shell to prevent its fracture and maintain stable contact with the electrolyte for improved cycle performance. Upper panel: Adapted with permission from Liu, X.H., *et al.*, 2011b. Ultrafast electrochemical lithiation of individual Si nanowire anodes. *Nano Letters* 11 (6), 2251–2258. Available at: <https://doi.org/10.1021/nl200412p>. Copyright (2011) American Chemical Society. Lower panel: Liu, X.H., *et al.*, 2012b. In situ atomic-scale imaging of electrochemical lithiation in silicon. *Nature Nanotechnology* 7 (11), 749–756. Available at: <https://doi.org/10.1038/nnano.2012.170>. [COPYRIGHT] (2012). Wang, Z., *et al.*, 2013b. Electron-rich driven electrochemical solid-state amorphization in Li–Si alloys. *Nano Letters* 13 (9), 4511–4516. Available at: <https://doi.org/10.1021/nl402429a>. Copyright (2013) American Chemical Society. Liu, X.H., *et al.*, 2012c. Size-dependent fracture of silicon nanoparticles during lithiation. *ACS Nano* 6 (2), 1522–1531. Available at: <https://doi.org/10.1021/nl204476h>. Copyright (2012) American Chemical Society. Liu, N., *et al.*, 2012a. A yolk-shell design for stabilized and scalable Li-ion battery alloy anodes. *Nano Letters* 12 (6), 3315–3321. Available at: <https://doi.org/10.1021/nl3014814>. Copyright (2012) American Chemical Society.

silicon nanowires were observed using IL electrolyte (Liu *et al.*, 2011b) involving huge volume expansion (Fig. 2(B), upper panel). It also confirmed the improved reaction rate by introducing a carbon coating on the surface to enhance the electrical conductivity. And using solid-electrolyte setup, much higher resolution was achieved and atomic-scale mechanism of the core-shell reaction involving layer-by-layer peeling of the silicon from the surface as lithiation propagates from the surface towards the core of the nanowire (Liu *et al.*, 2012b) as shown in Fig. 2(B) (lower panel). These observations provide direct evidence on how lithiation takes place in the materials, and the electron diffraction pattern (EDP) can be analysed to confirm the reaction products. In addition, EELS elemental mapping can be combined with STEM or EFTEM to directly determine the change in the elemental concentrations and understand how lithium migrates inside the nanowire causing a phase transformation (Wang *et al.*, 2013b) as shown in Fig. 2(C).

Although there are limitations for using electron microscopy (under high vacuum condition) to observe the electrochemical reactions in open-cell setups, the rich information on the reaction process in the smallest components of the battery system contributes to the development of novel design of the electrode materials. By directly observing the lithiation process of Si nanoparticles with different diameters, size-dependency on the mechanical stability of the particles under lithiation was revealed (Liu *et al.*, 2012c), which provide criteria of the particle size to ensure the cyclability of the material (Fig. 2(D)). Yolk-shell design with silicon core and carbon shell was demonstrated to achieve high capacity, long cycle life, and high efficiency, by accommodating the volume changes of silicon inside the shell, which was confined by in situ TEM observations (Liu *et al.*, 2012a). Similar concept was applied to other materials to enhance the performance of Al anode (Li *et al.*, 2015), cluster of Si-C structures with improved packing density (Liu *et al.*, 2014), and sulfur cathode for Li-S battery (Wei Seh *et al.*, 2013), to name a few.

Recently, the open-cell configuration has been extensively used to study electrochemical reactions of all-solid-state batteries (Yamamoto *et al.*, 2010; Meng *et al.*, 2011; Wang *et al.*, 2016b; Cheng *et al.*, 2020; Cheng *et al.*, 2021; Fawey *et al.*, 2020; Wang *et al.*, 2020b). Understanding the interfacial phenomena between the solid electrolyte and the electrode is important for optimizing the ionic conductivity and the battery performance. Oxide-type SE generally shows higher stability against Li, and LLZO exhibits the best resistance (Zhu *et al.*, 2016; Duan *et al.*, 2018). LIPON and sulfide-type SEs reacts with Li. However, the resulting interfacial layers have low electrical conductivity that limits continuous reactions (Kamaya *et al.*, 2011). These reactions are extremely difficult to observe because the interface is embedded in the battery cell. *In situ* TEM is an excellent tool to observe the reactions at the interfaces. Since no liquid electrolyte is used, the same condition within the actual device can be reproduced inside a TEM. Note, that the specimen needs to be electron beam transparent for TEM imaging, which limits the size-scale of the observation area.

Thin lamella containing cathode, electrolyte, and anode is extracted from a solid-state battery cell creating a micron-sized battery inside TEM as shown in Fig. 3(A)(a) (Wang *et al.*, 2016b). Using a LiCoO₂/LiPON/Si thin film battery, evolution of the interfacial layer between LiCoO₂ and LIPON was revealed. Fig. 3(A)(b) shows the change in the lithium concentration at the disordered LCO layer at the interface between ordered-LCO and the electrolyte. The EELS spectra in Fig. 3(A)(c) confirms the chemical change in Co-O bond at the interface after charging. These results suggests that chemical changes at the interface are responsible for the interfacial impedance, one of the limiting factors in ASSBs. Here, the EELS spectra and chemical composition mapping are different for *ex situ* and in situ analysis because of the short air exposure during the sample transfer between the instruments, which emphasizes the importance of in situ characterization in understanding the fundamental electrochemical mechanisms in nano-scales. Ma *et al.* (2016) reported that cubic LLZO SE reacts with Li in contact to form few unit cells of tetragonal LLZO at the interface (Fig. 3(B)). The tetragonal phase has lower lithium conductivity compared to the cubic phase. However, the phase is limited to only ~5 nm layer at the interface and does not propagate showing high stability of LLZO. Differential phase contrast STEM (DPC-STEM) technique can be combined with to reconstruct an electric field vector map and a charge-density map with high spatial resolutions (Zhang *et al.*, 2020a). Using this technique, Wang *et al.* (2020b) directly observe the interface lithium-ion accumulation resulting from the SCL by investigating the net-charge-density distribution across the electrode/electrolyte interface of a working sulfide-based ASSLIB using the in situ DPC-STEM technique. As shown in Fig. 3(C), change in the charge-density distribution at the LCO/LPSCI interface was clearly visualized at an extremely high resolution. These new findings from in situ TEM can lead to an advancement of the technology. For example, a Coble creep mechanism was discovered by Chen *et al.* (2020b) that directs Li deposition inside a carbonous tube. This phenomenon was used in the electrode/electrolyte design to prevent dendrite and stabilize SEI to enhance the cycle performance of the battery (Fig. 3(D)).

Close-Cell TEM

To analyse the reaction processes in actual battery operating environments, close-cell configurations were implemented to in situ TEM (Gu *et al.*, 2013; Ahn *et al.*, 2015; Liang *et al.*, 2015; Wu and Yao, 2015a; Zeng *et al.*, 2015; Hodnik *et al.*, 2016; Kushima *et al.*, 2017; Pu *et al.*, 2020). Here, microelectromechanical system (MEMS) micro-chips with electron-beam-transparent membrane windows and electrode leads are fabricated to confine the highly volatile electrolyte and prevent it from evaporating inside a TEM column. These chips are mounted on a specially designed TEM holder with a clamping mechanism and O-rings to confine the liquids for TEM observations without exposing the injected electrolytes to the vacuum as shown in Fig. 4(A) (Unocic *et al.*, 2014). The liquid-confining cell can also be mounted on a biasing holder after assembled to inject the electrolyte and sealing the perimeter to prevent the evaporation inside a TEM as shown in Fig. 4(B) (Kushima *et al.*, 2015; Kushima *et al.*, 2017). The thickness of the electrolyte layer inside the cell is controlled by the spacers deposited on the chips to allow electrolyte to reach the

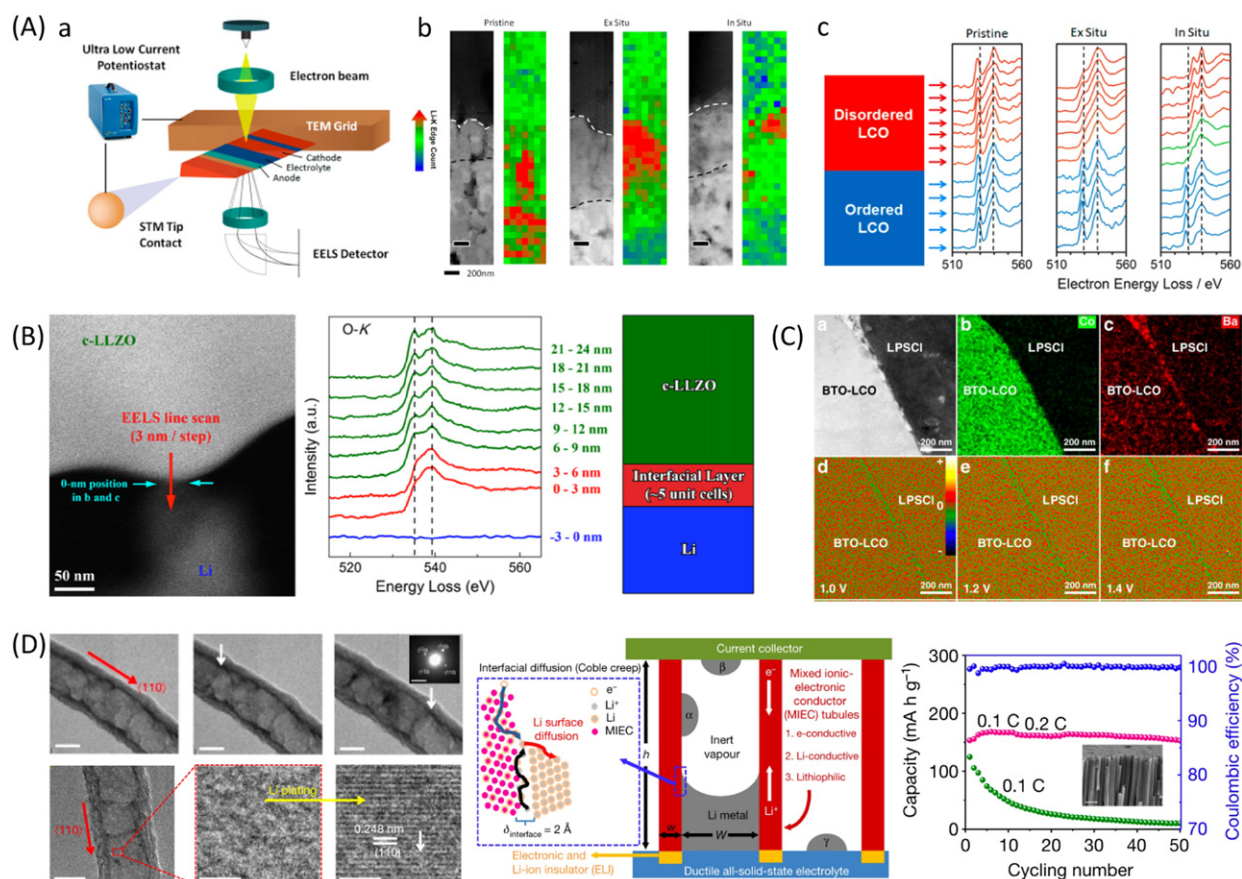


Fig. 3 Applications of in situ TEM in solid-state battery reactions. (A) a. Schematic of the experimental setup of nanobattery mounted on a TEM grid. The cathode is electrically connected to the grid and a piezo-controlled STM tip contacts the anode current collector. b. HAADF image of the nanobattery stack along with Li K-edge concentration mapping of pristine, ex situ, and in situ samples. c. O K-edge from the disordered LCO layer (red) and ordered LCO layer (blue) for pristine, ex situ, and in situ samples. The green spectra are O K-edge from the interface between disordered and ordered LCO. (B) HAADF-STEM image of crystal LLZO in contact with Li, O K-edges obtained in the EELS line scan indicated in the STEM image, and schematic illustration of the interfacial behavior suggested by the EELS line scan. (C) HAADF-STEM image of the BTO-LCO/LPSCI interface and corresponding mappings of Co and Ba elements (upper panel), and *In situ* DPC-STEM observations of net-charge-density accumulation at the BTO-LCO/LPSCI interface with different bias voltages. The color bar indicates the relative magnitude of the positive/negative charge density. (D) Coble creep infiltrating of lithium metal inside a carbon tubule to improve the cycle performance of Li metal anode. Adapted with permission from Wang, Z., *et al.*, 2016b. In Situ STEM-EELS observation of nanoscale interfacial phenomena in all-solid-state batteries. *Nano Letters* 16 (6), 3760–3767. Available at: <https://doi.org/10.1021/acs.nanolett.6b01119>. Copyright 2016 American Chemical Society. Ma, C., *et al.*, 2016. Interfacial stability of Li metal–solid electrolyte elucidated via In Situ electron microscopy. *Nano Letters* 16 (11), 7030–7036. Available at: <https://doi.org/10.1021/acs.nanolett.6b03223>. Copyright 2016 American Chemical Society. Wang, L., *et al.*, 2020b. In-situ visualization of the space-charge-layer effect on interfacial lithium-ion transport in all-solid-state batteries. *Nature Communications* 11 (1), 5889. Available at: <https://doi.org/10.1038/s41467-020-19726-5>. With CC-BY. Chen, Y., *et al.*, 2020b. Li metal deposition and stripping in a solid-state battery via Coble creep. *Nature* 578 (7794), 251–255. Available at: <https://doi.org/10.1038/s41586-020-1972-y>. [COPYRIGHT] (2020).

viewing area while maintaining the overall electron-beam transparency. To restrict the reaction at the viewing window, the electrode outside of the area is typically insulated. An ability of close-cell TEM technique opened a new area of studies to directly observe the nano-scale phenomena at interfaces between solid, liquid and gas.

Gu *et al.* (2013) demonstrated the first application of in situ liquid-cell TEM to observe the battery electrode reaction in a liquid electrolyte, successfully visualizing a lithiation/delithiation process of a single Si nanowire electrode in a real battery configuration with an liquid electrolyte. The use of close-cell TEM enables the studies of important electrochemical events occurring at the electrolyte-electrode interface in Li-ion battery such as SEI formation and dendritic growth of lithium at a high charge rate. Zeng *et al.* (2014) used a gold electrode with LiPF₆/EC/DEC electrolyte and observed the process of SEI formation and subsequent lithium dendrite nucleation with a uniform development of the SEI on the electrode as shown in Fig. 4(C). On the other hand, Sacci *et al.* (2014) observed a dendritic SEI on a gold electrode prior to dendritic growth of lithium when paired with a different electrolyte (LiPF₆/EC/DMC) as shown in Fig. 4(D), indicating the electrolyte compositions have a huge impact on the morphology of the SEI and plating behavior of lithium. These early implementations of the liquid-cell TEM provided insights into kinetics of SEI formation and its morphological development. However, it is still a challenge to fully understand the SEI evolution because of the low spatial

resolutions with the presence of liquid interfering with the electron beam. Hou *et al.* (2019) used HAADF-/ADF-STEM with sub-nanoscale mass-sensitive contrast to analyze the formation, growth and failure of SEI films on a gold electrode. As shown in Fig. 4(E) (upper panels), sequential HAADF-STEM images revealed a development of the double-layer SEI structure with inner layer consisting of compact inorganic products and the outer layer with low-density organic products from the electrolyte reduction. The electrolyte permeated through the porous outer layer and the SEI was continuously developed until the inner layer reached a certain thickness and uniformity to passivate the electrode surface, followed by the lithiation of the gold electrode. This hybrid organic-inorganic SEI layer was further studied using ADF-STEM with better capability to analyze the light elements by taking both diffraction and mass contrasts. As shown in Fig. 4(E) (lower panels), non-uniform development of SEI on the surface and the localized lithiation of the gold electrode was observed leading to the large volume expansion and stretching/breaking of the SEI. These multi-component/layered SEI structures have been proposed (Cheng *et al.*, 2016; Peled and Menkin, 2017). The mass-contrast imaging by in situ HAADF/ADF-STEM provided direct evidence of the dynamic formation and evolution of the double-layered SEI film.

Nucleation and growth of metal dendrites have been studied using close-cell in situ TEM (White *et al.*, 2012; Sun *et al.*, 2013; Mehdi *et al.*, 2015; Kushima *et al.*, 2017; Beker *et al.*, 2020). Mehdi *et al.* successfully observed Li deposition and dissolution processes at the interface between the Pt working electrode and the LiPF₆/PC electrolyte (Mehdi *et al.*, 2015). Fig. 4(F) shows the first lithium deposition and dissolution process. The sequential images during charge/discharge clearly show the formation of the SEI layer, alloying of Pt electrode with Li⁺ insertion, and the detachment of lithium flakes from the electrode during the dissolution step. The “dead Li” no longer attached to the Pt electrode did not participate in the subsequent charge/discharge cycles causing an irreversible capacity loss. These images showing the electrodeposition/stripping of Li metal and the evolution of the SEI layer were correlated with the simultaneously acquired cyclic voltammograms to quantify the electrodeposition, and electrolyte breakdown processes in nanoscales. Although lithium dendrites were believed to grow from the tip, they are reported to grow also from the “root” (Dollé *et al.*, 2002; Steiger *et al.*, 2014a, Steiger *et al.*, 2014b; Bai *et al.*, 2016). Variety of factors can affect the growth mode (Yoshimatsu *et al.*, 1988; Arakawa *et al.*, 1993a; Arakawa *et al.*, 1993b; Yamaki *et al.*, 1998; Steiger *et al.*, 2014a): current density, electrolyte composition and concentration, temperature, SEI structure, etc. By observing an initial nucleation and growth of dendrites using in situ liquid-cell TEM, Kushima *et al.* (2017) revealed the essential roles of the liquid electrolyte decomposition reaction and SEI formation in the growth mode selection. At high current density or high overpotential, a small spherical lithium domain first develops on the surface of the electrode and then start to evolve into long whiskers that grow like hair from the root at the electrode interface (Fig. 4(G)), in contrast to the tip growth of conventional dendrites. For typical operating currents, the growth and dissolution of Li “whiskers (root growth)” and/or “mossy (tip growth)” deposits are modulated by short-range solid-state diffusion through the passivating SEI layer.

High-resolution imaging with a liquid-cell TEM is challenging because of the extra layers of the membrane window and the confined liquid. Here, graphene-based liquid cell (GLC) in situ TEM technique has advantages over silicon-microfluidic cells because it relies only on layers of graphene that wrap around the samples (including surrounding liquid and/or gas) to protect them from the high vacuum environment inside TEM (Ghodsi *et al.*, 2019; Park *et al.*, 2021). The graphene layers with thickness below 1 nm minimizes electron beam scattering and contributes to improved imaging resolution, and its impermeability of liquid/gas molecules prevents their leakage inside TEM. GLC technique found its applications to observing particle dynamics in liquids (Yuk *et al.*, 2012; De Clercq *et al.*, 2014; Jeong *et al.*, 2015; Park *et al.*, 2015a; Hutzler *et al.*, 2018), biological structure/dynamics (Park *et al.*, 2015b; Wojcik *et al.*, 2015; Dahmke *et al.*, 2017; Wang *et al.*, 2020a), and, of course, electrochemical reactions (Yuk *et al.*, 2014; Cheong *et al.*, 2016; Seo *et al.*, 2019; Xu *et al.*, 2019). GLCs can be prepared by simply sandwiching the samples and liquid using two TEM grids with graphene membranes, and a small amount of liquid is trapped between the two graphene layers as shown in Fig. 4(H) (Zhang *et al.*, 2017). Since most GLCs are made with TEM grids, regular TEM holders can be used for the experiments without needing to use specially made in situ holders or silicon-microfluidic cells. Even without a biasing holder, electron beam can be used for electron supply and facilitate electrochemical reactions (Yuk *et al.*, 2014). Because of its ability to obtain high resolution images, GLCs can also be used for studying SEI dynamics. For example, Cheong *et al.* (2016) used a GLC to directly observe the growth of a stable SEI layer on SnO₂ nanotubes. Fig. 4(I) shows the development of SEI layer on the surface. First, an uneven layer was formed as agglomerates of decomposed electrolytes diffused into the layer, and later became more uniform layer as it undergoes stabilization phase. The growth dynamics of SEI was clearly visualized with GLC. The use of GLC opens new and alternative opportunities to observe different interfacial phenomena at extremely fine scales, which is a challenge using silicon-microfluidic cells.

The close-cell TEM can also be used for observing reactions involving gas phases (Wu and Yao, 2015b; Wu *et al.*, 2016). Use of an environmental TEM (ETEM) with differential pumping (DP) system is also an option. However, the working pressure for the state-of-the-art DP-ETEMs is limited to 15–20 Torr depending on the molecular weight of the gases (Mehraeen *et al.*, 2013), and the additional differential pumping aperture placed below the specimen blocks the high-angle scattered beams limiting the ADF-STEM and analysis of high-angular diffraction phenomena, which are important features for studying electrochemical reactions in energy materials. Therefore, this review focuses on the application of close-cell TEM for studying gas-phase reactions. Fig. 5(A) shows a typical “nanoreactor” gas-flow holder with a heating element (Creemer *et al.*, 2008). The integrated heating element on the membrane window using a MEMS-based technique enabled limits the thermal expansion of the system components reducing the specimen drift. This type of MEMS-based window with integrated heater is gaining popularity compared with conventional gas-flow holder with much bulkier furnace heater (Yaguchi *et al.*, 2011) causing huge thermal drift during heating/cooling. The technique enables the direct observations of catalytic reactions important for understanding the ORR and OER reactions in fuel cells. Vendelbo *et al.* (2014) employed a gas-flow cell and a nanoreactor coupled with mass spectrometry and calorimetry to study the oscillatory CO oxidation catalyzed by Pt nanoparticles, and the observation revealed that the oscillatory CO conversion reaction was synchronized with a periodic shape changes of the Pt nanoparticles as shown in Fig. 5(B). Shen *et al.* (2019) observed

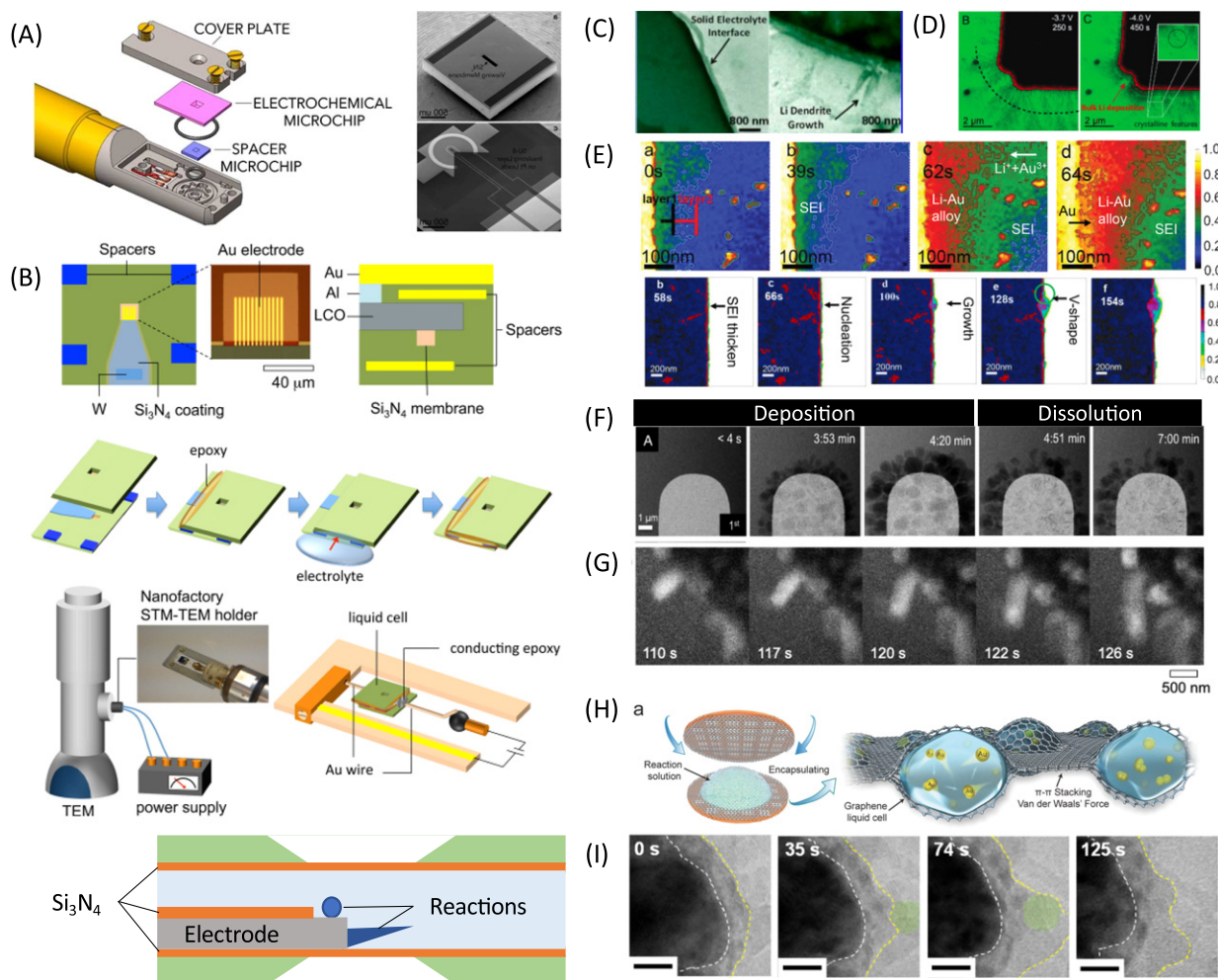


Fig. 4 (A) Schematic illustration of a close-cell in-situ TEM holder with micrograph of the silicon micro-fluidic cell. (B) Schematic illustration of a liquid-confining cell, its assembly process, and mounting configuration on a in situ biasing holder. Cross-section view of the cell near the viewing windows is also shown. (C) SEI and lithium dendrite formations observed using liquid-cell TEM. (D) Amorphization of SEI dendrites by Li deposition (left) and Li deposition/SEI layer formation at constant potential (right) observed by liquid-cell in situ TEM. (E) Time sequential high-magnification HAADF-STEM images of SEI film (upper panel) and time sequential ABF-STEM images showing the morphology variation of the SEI film and interaction between SEI film and intercalated Au electrode (lower panel). (F) HAADF images of Li deposition and dissolution at the interface between the Pt working electrode and the LiPF₆/PC electrolyte. (G) Root growth of lithium dendrites captured by in situ TEM. (H) Schematic illustration of the fabrication process of a graphene liquid cell. (I) Evolution of the SEI layer on the surface of SnO₂ nanotube during lithiation analyzed by TEM using GLC. Scale bar is 10 nm. Reproduced with permission from Unocic, R.R., *et al.*, 2014. Quantitative electrochemical measurements using In Situ ec-S/TEM devices. *Microscopy and Microanalysis* 20 (2), 452–461. Available at: <https://doi.org/10.1017/S1431927614000166>. Copyright © Microscopy Society of America 2014. Kushima, A., *et al.*, 2015. Charging/discharging nanomorphology asymmetry and rate-dependent capacity degradation in Li–oxygen battery. *Nano Letters* 15 (12), 8260–8265. Available at: <https://doi.org/10.1021/acs.nanolett.5b03812>. Copyright 2015 American Chemical Society. Zeng, Z., *et al.*, 2014. Visualization of electrode–electrolyte interfaces in LiPF₆/EC/DEC electrolyte for lithium ion batteries via In Situ TEM. *Nano Letters* 14 (4), 1745–1750. Available at: <https://doi.org/10.1021/nl403922u>. Not subject to U.S. Copyright. Sacchi, R.L., *et al.*, 2014. Direct visualization of initial SEI morphology and growth kinetics during lithium deposition by in situ electrochemical transmission electron microscopy. *Chemical Communications* 50 (17), 2104–2107. Available at: <https://doi.org/10.1039/C3CC49029G>. Copyright 2014 Royal Society of Chemistry. Hou, C., *et al.*, 2019. Operando observations of SEI film evolution by mass-sensitive scanning electron microscopy. *Advanced Energy Materials* 9 (45), 1902675. Available at: <https://doi.org/10.1002/aenm.201902675>. Copyright 2019 WILEY-VCH Verlag GmbH & Co. Mehdi, B.L., *et al.*, 2015. Observation and quantification of nanoscale processes in lithium batteries by operando electrochemical (S)TEM. *Nano Letters* 15 (3), 2168–2173. Available at: <https://doi.org/10.1021/acs.nanolett.5b00175>. Copyright 2015 American Chemical Society. Kushima, A., *et al.*, 2017. Liquid cell transmission electron microscopy observation of lithium metal growth and dissolution: Root growth, dead lithium and lithium flocs. *Nano Energy* 32, 271–279. Available at: <https://doi.org/10.1016/j.nanoen.2016.12.001>. Zhang, J., *et al.*, 2017. Clean transfer of large graphene single crystals for high-intactness suspended membranes and liquid cells. *Advanced Materials* 29 (26), 1700639. Available at: <https://doi.org/10.1002/adma.201700639>. Copyright 2017 WILEY-VCH Verlag GmbH & Co. Cheong, J.Y., *et al.*, 2016. Growth dynamics of solid electrolyte interphase layer on SnO₂ nanotubes realized by graphene liquid cell electron microscopy. *Nano Energy* 25, 154–160. Available at: <https://doi.org/10.1016/j.nanoen.2016.04.040>. Copyright 2016 Elsevier Ltd.

atomic-scale elemental diffusion and surface reconstruction of ternary octahedral Pt_2CuNi alloy nanoparticles in an oxidative environment at elevated temperatures. Combined with Z-contrast images with BF-STEM, the atomic-scale surface oxidation mechanism was captured as shown in Fig. 5(C). Gas-phase reactions can also be observed using liquid-cell TEM. By bubbling oxygen in the electrolyte before injecting it to the liquid-confining cell, Kushima *et al.* (2015) observed LAB reactions under TEM and confirmed asymmetric reactions leading to a detachment of reaction product from the electrode causing irreversible capacity loss as shown in Fig. 5(D).

As explained above, close-cell TEM enables the observation of nano-scale phenomena in actual working environment contributing to the deeper understanding of the fundamental science in nano-scale spatial resolutions. However, care must be taken since the electron beam can interact with the enclosed liquid/gas resulting in undesired side reactions including, radiolysis (Pastina and LaVerne, 2001; Joseph *et al.*, 2008), bubbling (Grogan *et al.*, 2014; Schneider *et al.*, 2014), chemical reactions from ionized of gas/liquid molecules (Simonsen *et al.*, 2010; Kuwauchi *et al.*, 2012), reduction and precipitation of nanoparticles from solution (Evans *et al.*, 2011; den Heijer *et al.*, 2014; Nielsen *et al.*, 2014), etc. While little effect on the image resolution is observed for gas (Xin *et al.*, 2013), the presence of liquid has significant impacts with many affecting parameters such as liquid thickness, electron beam energy/dosage, and imaging mode (de Jonge and Ross, 2011). The examples of the electron beam effect in closed-cell TEM and the TEM/STEM resolutions for imaging materials in liquid-cell is summarized in Fig. 6.

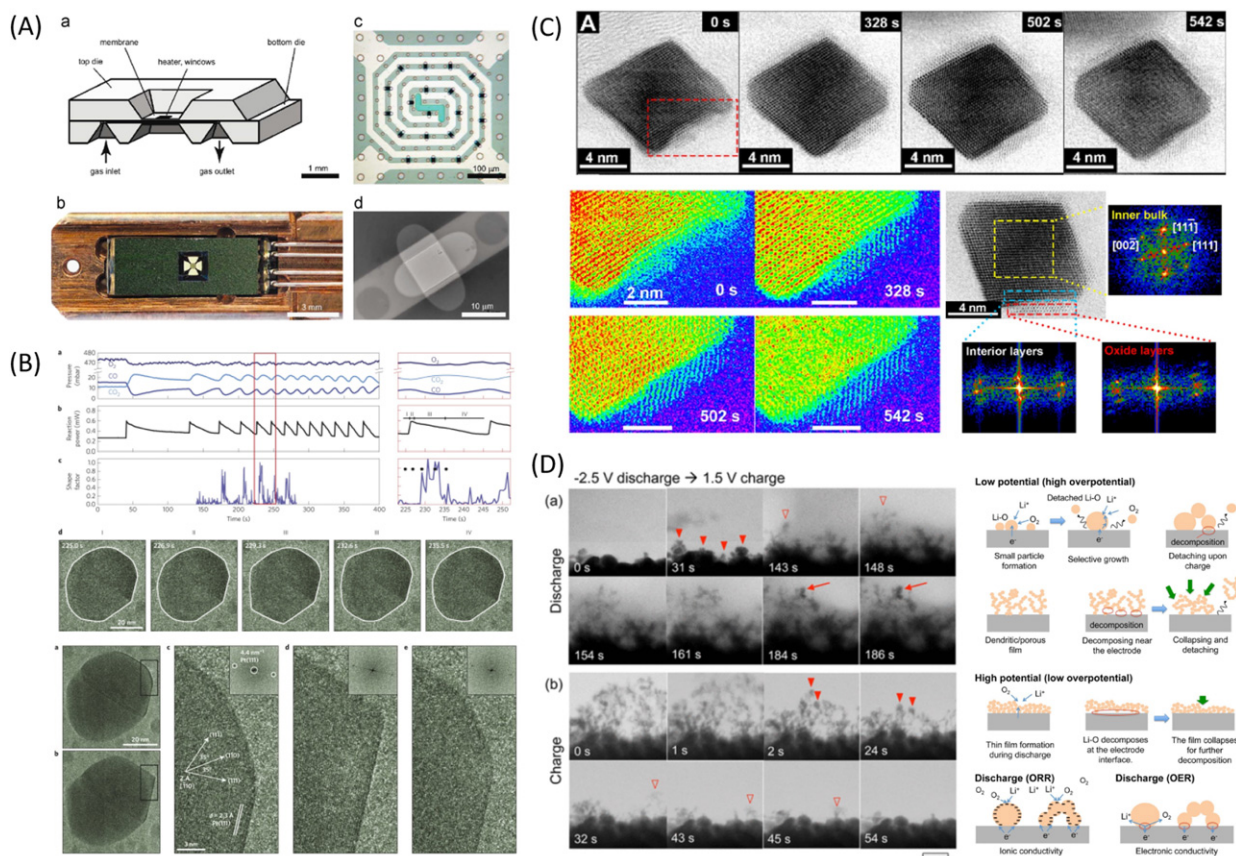


Fig. 5 (A) In situ gas flow holder with heating nanoreactor. (B) Mass spectrometry of the CO , O_2 and CO_2 pressures, reaction power, and shape factor for the Pt nanoparticle as a function of time obtained from the sequential time-resolved TEM images of a Pt nanoparticle at the gas exit of the reaction zone. The HRTEM images show the more spherical shape and the more faceted shape, during the oscillatory reaction. Fast Fourier transforms included as insets in reveal a lattice spacing corresponding to the Pt(111) lattice planes. (C) Sequential in situ bright-field images of the Pt_2CuNi octahedral nanoparticle exposed to the oxidative condition along with false-color BF-STEM images of one representative (111) facet showing oxidative evolution. FFT analysis the particle confirms a good FCC crystal structure in the inner bulk region with a typical sixfold diffraction point. (D) Sequential micrographs of the discharge (ORR) and charge (OER) reactions in LAB observed by liquid-cell TEM, and schematic illustration explaining the discharge/charge mechanism in the Li– O_2 battery. Reprinted from Creemer, J.F., *et al.*, 2008. Atomic-scale electron microscopy at ambient pressure. *Ultramicroscopy* 108 (9), 993–998. Available at: <https://doi.org/10.1016/j.ultramicro.2008.04.014>. With permission from Elsevier/Vendelbo, S.B., *et al.*, 2014. Visualization of oscillatory behaviour of Pt nanoparticles catalysing CO oxidation. *Nature Materials* 13 (9), 884–890. Available at: <https://doi.org/10.1038/nmat4033>. [COPYRIGHT] (2014). Shen, X., *et al.*, 2019. Oxidation-induced atom diffusion and surface restructuring in faceted ternary Pt–Cu–Ni nanoparticles. *Chemistry of Materials* 31 (5), 1720–1728. Available at: <https://doi.org/10.1021/acs.chemmater.8b05199>. Copyright 2019 American Chemical Society. Kushima, A., *et al.*, 2015. Charging/discharging nanomorphology asymmetry and rate-dependent capacity degradation in Li–oxygen battery. *Nano Letters* 15 (12), 8260–8265. Available at: <https://doi.org/10.1021/acs.nanolett.5b03812>. Copyright 2015 American Chemical Society.

SEM

High depth of field and resolution in nano-scales make SEM a potent instrument for capturing the electrochemical reaction processes and comprehending the fundamental mechanisms and kinetics of materials. Although SEM cannot reach the resolutions of TEM, its ability to capture the 3D profile of the sample morphologies enables materials characterizations from different aspects. However, SEM also suffers from a fundamental challenge. For stable and high-resolution imaging, SEM requires a high vacuum and conductive sample surface. Consequently, conventional electrolytes are not suitable for in situ SEM analysis. Several attempts to understand the evolutions of electrolytes have been made (Baudry, 1988; Orsini *et al.*, 1998; Raimann *et al.*, 2006). Baudry and Armand were the first to experiment with the in situ SEM to observe the morphological changes in FeS, TiS₂, and V₆O₁₃ electrodes during the lithiations using polymer electrolytes (Baudry, 1988). The samples required heating to increase their discharge rate because of the slow ionic transport within the polymer electrolyte, and they were exposed to the atmosphere for about 30 s during the transfer process leading to surface contamination. However, the method successfully captured the different reaction behavior and the stability of these materials in nano-scale. Orsini *et al.* (1998) resolved the issue of surface contamination due to environment exposure by transferring the cell from a glove box to SEM chamber using a specially designed movable airlock system. To prevent any damage or electrolyte evaporation caused by the vacuum in the SEM chamber, after the battery was cycled several times and cooled to -20°C . However, the battery couldn't be cycled inside the SEM chamber due to the cooling. Raimann *et al.* (2006) took another approach by using an environmental scanning electron microscope (ESEM) for in situ observation of a liquid electrolyte. ESEM facilitated the experiments using electrolytes with high vapor pressure. Nevertheless, the experiment's resolution was limited by the strong electron scattering effect of ionic gas and the experimentation must be done swiftly due to electrolyte evaporation.

To alleviate the limitations corresponding to the compatibility of electrolytes in an SEM chamber which requires vacuum conditions, observing electrode performance through in situ SEM has recently become more prevalent using ionic liquid electrolytes. (Arimoto *et al.*, 2008; Chen *et al.*, 2011, 2016; Tsuda *et al.*, 2015, Tsuda *et al.*, 2019; Shi *et al.*, 2019). Ionic liquids have negligible vapor pressure and take a long time to evaporate even under a high vacuum condition inside SEM. ILs have also been reported to have wide electrochemical windows and high ionic conductivities (Ohno, 2005), making them a suitable candidate for in situ SEM observation (Earle *et al.*, 2006). Kuwabata *et al.* (2006) reported that ionic liquid electrolytes can be observed via in situ SEM without electron charge accumulation. Arimoto *et al.* (2008) designed an electrochemical system using an FTO-glass electrode and ionic liquid, where they observed the real-time evolution of the electrode-electrolyte interface and the gradual growth of dendrites. Chen *et al.* designed an ionic liquid electrolyte-based test cell combined with lithium and SnO₂ to observe the lithiation process. For the SnO₂ particles with small diameter in the order of 100 nm, a continuous Li₂O layer was formed on the surface and completely confined the particle. On the other hand, larger particles showed extrusions and cracks indicating inhomogeneous lithiations (Chen *et al.*, 2011).

Although SEM cannot achieve TEM resolutions, an advantage of using SEM is the ability to observe 3D structure of the material. For example, a single Sn particle was immersed in the IL electrolyte and its structural change was observed during the battery operation as shown in Fig. 7(A) (Zhou *et al.*, 2019). After extracting the particles at different charge/discharge states (Fig. 7(Aa)), focused ion beam (FIB) was used to cut the particle to observe the internal structure (Fig. 7(Ab-g)), and the volume changes and cracking of the micron-sized particles were observed. Open-cell environment in SEM is also suitable for observing reactions in all-solid-state batteries (Nagao *et al.*, 2013; Golozar *et al.*, 2019, p. ; Cui *et al.*, 2022). Nagao *et al.* (2013) used SEM to observe the interface between a chamfered stainless steel current collector and Li₂S–P₂S₅ SE and confirmed a cracking of the SE and penetration of lithium along the grain boundaries at high current density above 1 mA/cm². As shown in Fig. 7(B), cracking of the SE surface was clearly observed after the cell was shorted.

Close-cell configurations can also be integrated in SEM. Unlike TEM, where specimen and “nano” battery constructed inside TEM are too small compared to the real battery, SEM allows observations of electrochemical reactions in the larger cells close to actual battery sizes. Rong *et al.* (2017) developed an in situ electrochemical SEM (EC-SEM) method using a liquid cell to systematically study the lithium plating/stripping process. As shown in the schematics of Fig. 7(C), EC-SEM cell consists of two chips with the top chip having silicon nitride membrane viewing window and the bottom chip with electrolyte filling holes. The electrodes are patterned on the top chip with a micro-gap positioned at the viewing window. It enabled the direct observations of the SEI evolution, lithium dendrite nucleation/growth, and the stripping process forming “dead” lithium fragments (Fig. 7(C)). Comparing the lithium plating/stripping behaviors with different additives, the roles of LiNO₃ and Li₂S₈ additives and the synergetic effect to prevent lithium dendrites in Li-S battery using LiTFSI/DOL/DME electrolyte were revealed.

Other In Situ/Operando Techniques

Optical Microscopy

Understanding the fundamental reaction mechanisms of energy storage materials requires the tracking of the dynamic processes during the battery operation. Various nondestructive in situ techniques have been developed to monitor the electrochemical reactions under different stages of operation as described above. However, these techniques are limited to specific chemical species, requiring sophisticated instrumentation, and/or complex designs for the experimental setups. On the other hand, in situ optical microscopy (OM) offers some flexibility toward these issues as shown in Fig. 8 (Harris *et al.*, 2010; Sethuraman *et al.*, 2010; Aryanfar *et al.*, 2014; Bai *et al.*, 2016; Sun *et al.*, 2021) although its resolution is limited by the abbe diffraction limit (Stelzer, 2002). The technique has been used to study variety of energy storage systems (Chen *et al.*, 2020a).

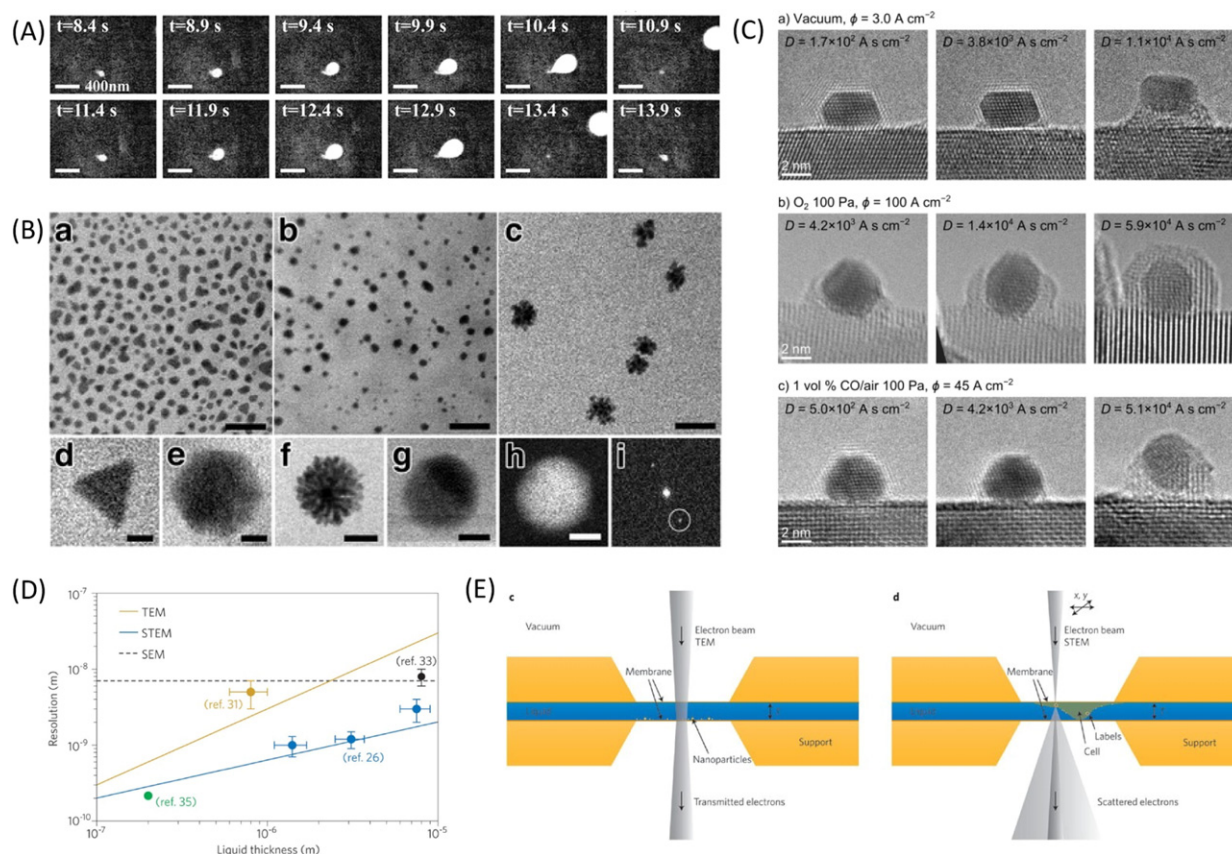


Fig. 6 Beam effect in closed-cell TEM with liquid/gas and TEM/STEM resolution with liquid. (A) Closed-cell TEM observation of electron beam induced bubble nucleation on the membrane, growth, and detachment followed by another bubble repeating the process of nucleation/growth/detachment at the same spot. (B) Nanoparticle growth under varying chemical composition of parent solution by electron beam irradiation. (C) Structural reorganization processes of Au nanoparticle on TiO_2 under electron irradiation (current density ϕ) in vacuum, O_2 , and Co/air environment. (D) Theoretical maximal resolution versus water thickness for TEM, STEM and SEM calculated for typical TEM/STEM instrument parameters at 200 keV beam energy, and for the imaging of Au nanoparticles at the bottom of a layer of water for TEM, and at the top of the layer for STEM. (E) Schematics of TEM imaging of nanoparticles in a liquid fully enclosed between electron transparent windows (left) and STEM imaging of nanoparticle labels on whole biological cells (right). Adapted with permission from Grogan, J.M., *et al.*, 2014. Bubble and pattern formation in liquid induced by an electron beam. *Nano Letters* 14 (1), 359–364. Available at: <https://doi.org/10.1021/nl404169a>. Copyright © 2014, American Chemical Society. Evans, J.E., *et al.*, 2011. Controlled growth of nanoparticles from solution with In Situ liquid transmission electron microscopy. *Nano Letters* 11 (7), 2809–2813. Available at: <https://doi.org/10.1021/nl201166k>. Copyright 2011 American Chemical Society. Kuwauchi, Y., *et al.*, 2012. Intrinsic catalytic structure of gold nanoparticles supported on TiO_2 . *Angewandte Chemie International Edition* 51 (31), 7729–7733. Available at: <https://doi.org/10.1002/anie.201201283>. Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. de Jonge, N., Ross, F.M., 2011. Electron microscopy of specimens in liquid. *Nature Nanotechnology* 6 (11), 695–704. Available at: <https://doi.org/10.1038/nnano.2011.161>. Copyright 2011 with permission from Springer Nature.

One of the first in situ optical tests of Li transport was studied by Harris *et al.* (2010). Using a half-cell with a quartz viewing window, motions of the lithiation front in the graphite electrode was captured as shown in Fig. 8(A). The change in the color of the graphite electrode provides a semi-quantitative measure of the state of charge. A transparent coin-cell was designed by Aryanfar *et al.* (2014) to observe a cross-sectional view of the cell to study the deposition of lithium as shown in Fig. 8(B), providing a unique quantification method for the amount of dead lithium crystals produced by sequences of galvanostatic charge–discharge cycles. A simple capillary cell was developed by Bai *et al.* (2016) to observe the lithium growth process. They captured a change of the growth mechanism from root-growing mossy lithium to tip-growing dendritic lithium at the onset of electrolyte diffusion limitation (Fig. 8(C)). In situ OM is also capable of studying all-solid-state battery reactions. Sun *et al.* (2021) observed a nucleation and growth of Li within the solid-state electrolyte and revealed the crack initiation and formation during Li penetration during charging attributed to volume expansion.

Because of its simple experimental setup, in situ OM can be easily coupled with development of new strategies to improve the battery performance by confirming their working principles (Banik and Akolkar, 2015; Alaboina *et al.*, 2018; Wan *et al.*, 2018; Xiao *et al.*, 2020). For example, Wu *et al.* (2014) developed a bifunctional separator by stacking two polymer separators. One of the separators is coated with copper to make it conductive, which enables an early detection of dendrites before they reach the opposite electrode (Fig. 8(E)). Here, in situ optical observation was able to verify the functionality of the cell by monitoring the potentials during cycling. As shown in the figure, a simple transparent pouch cell was used for the in situ OM observations.

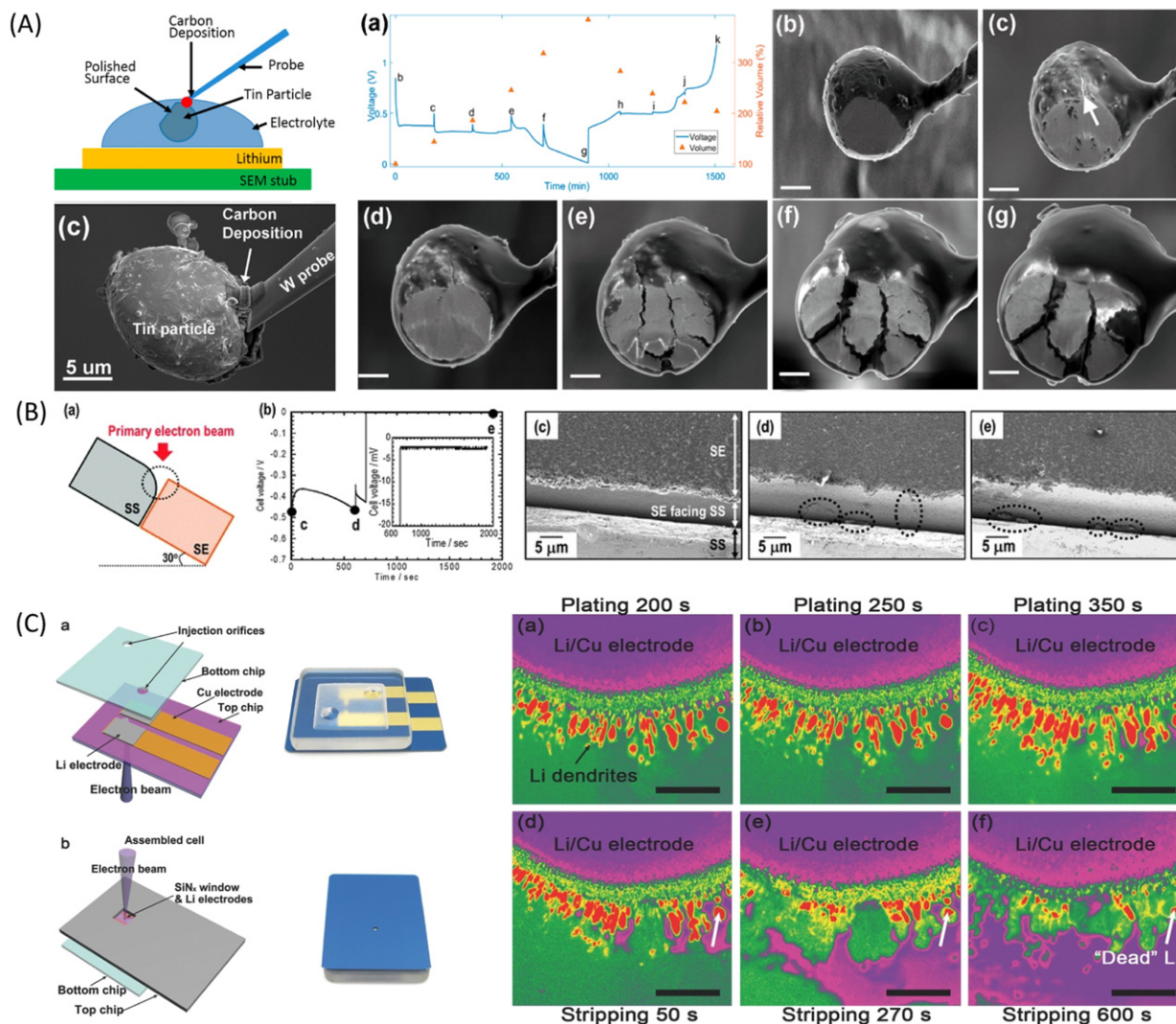


Fig. 7 (A) Schematic of in situ SEM set up of a single Sn particle battery, voltage profile and relative volume of the first cycle (charged at 0.3 nA), and SEM images of Sn particle corresponding to the different discharge states in (a). (B) Schematic of the all-solid-state cell for the in situ SEM observation with the stage tilted to an angle of 30 degrees, lithium deposition curves of the all-solid-state cells Li-80Li₂S · 20 P₂S₅ SE-SS at 2 mA/cm², and SEM images of the interface between the SE layer and SS at different positions of the same cell before (c) and after lithium deposition for 600 s (d) and 1920s (e). (C) Schematic illustration and the optical micrograph of the EC-SEM liquid cell (left) and first cycle of lithium plating/stripping processes using the LiTFSI/DOL/DME electrolyte with the additive of 1 wt% LiNO₃ (1 right). Adapted with permission from Zhou, X., *et al.*, 2019. In Situ focused ion beam scanning electron microscope study of microstructural evolution of single tin particle anode for Li-ion batteries. *ACS Applied Materials & Interfaces* 11 (2), 1733–1738. Available at: <https://doi.org/10.1021/acsami.8b13981>. Copyright 2019 American Chemical Society. Nagao, M., *et al.*, 2013. In situ SEM study of a lithium deposition and dissolution mechanism in a bulk-type solid-state cell with a Li₂S–P₂S₅ solid electrolyte. *Physical Chemistry Chemical Physics* 15 (42), 18600–18606. Available at: <https://doi.org/10.1039/C3CP51059J>. Rong, G., *et al.*, 2017. Liquid-phase electrochemical scanning electron microscopy for In Situ investigation of lithium dendrite growth and dissolution. *Advanced Materials* 29 (13), 1606187. Available at: <https://doi.org/10.1002/adma.201606187>. Copyright © 2017 WILEY-VCH Verlag GmbH & Co.

Atomic Force Microscopy

AFM is another useful tool for in situ/operando studies of the electrochemical reactions (Zhang *et al.*, 2021). In situ AFM requires a relatively simple experimental setup to obtain a 3-D topographic image using a cantilever probe with a sharp tip. Since AFM equipment is relatively portable, experiments can be performed inside the glovebox. Inaba *et al.* used an open cell approach inside the glovebox to study the morphological changes during SEI formation by using highly oriented pyrolytic graphite as shown in Fig. 9(A) (Jeong *et al.*, 2001; Inaba *et al.*, 2011). It revealed two different processes involved in SEI formation on graphite negative electrode: (1) Formations of hill-like structures and blistering on the surface of the HOPG were observed during first CV cycle from the accumulation of decomposition products of solvated lithium ions between graphite layers; and (2) Formation of a precipitation layer on the basal plane at lower potential from direct decomposition of solvents. These changes in the surface morphology were only observed in the first cycle indicating the surface was completely passivated to prevent further

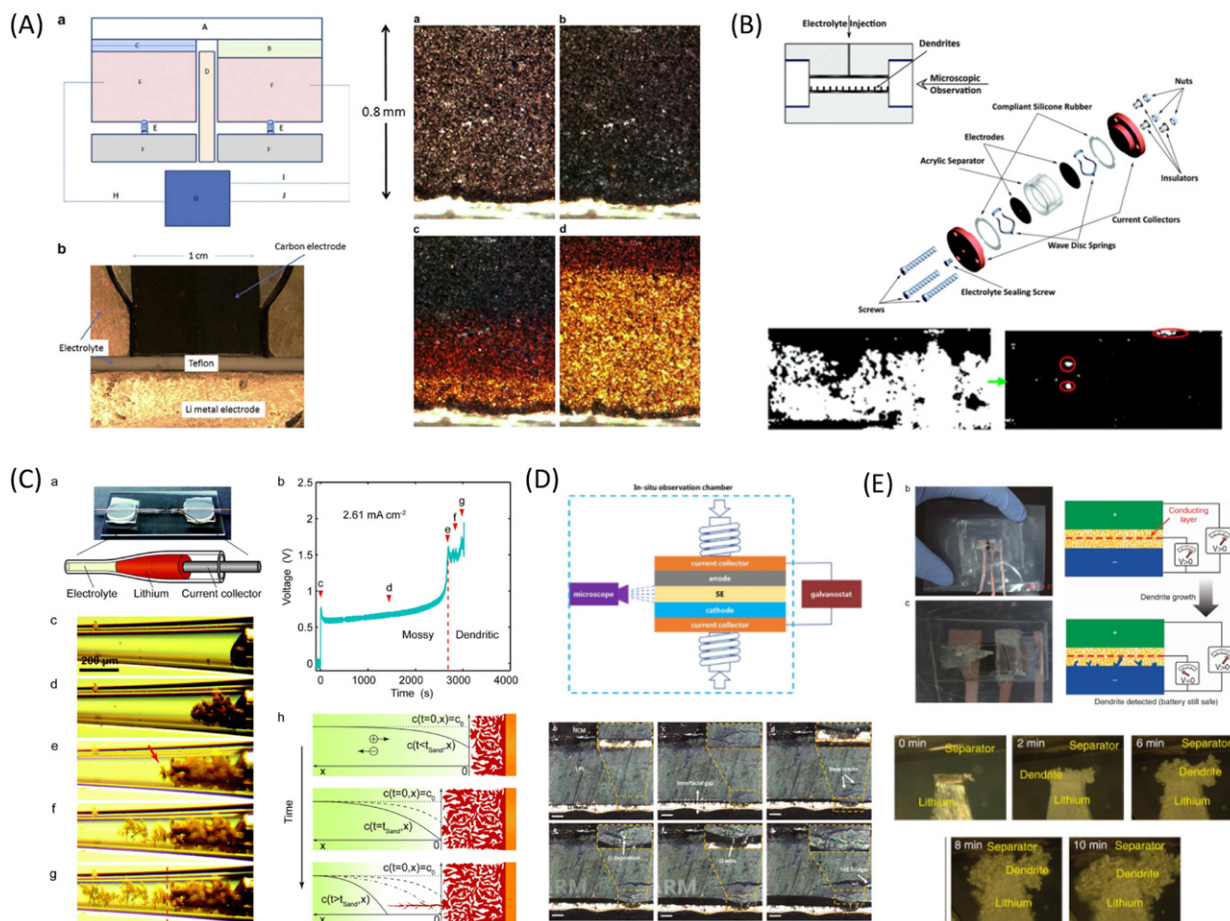


Fig. 8 (A) Side view schematic of the optical half-cell and photograph of the graphite electrode positioned about 2 mm from a Li metal electrode on electrically separated stainless steel supports (left) and a sequence of four optical micrographs showing the time-evolution of color in the electrode (right). (B) Schematic illustration of the transparent coin-cell for in situ OM (upper panel) and binary images of lithium electrodeposition showing dead lithium crystals marked by the red enclosures (lower panels). (C) In situ observations of lithium electrodeposition in a glass capillary filled with an electrolyte solution consisting of 1 M LiPF_6 in EC/DMC. Photo of the capillary cell (a), voltage responses of the capillary cell at a deposition current density of 2.61 mA cm^{-2} (b), in situ snapshots of the growth of lithium during the electrodeposition (c–g), and theoretical interpretation of the growth mechanisms of lithium electrodeposition during concentration polarization (h). (D) Schematic illustration of the experimental set-up of in situ OM observations of Li/LPS/NCM cell (upper panel) and cross-sectional snapshots of the cell taken during the charging process (lower panel). Scale bars are $100 \mu\text{m}$. The battery is kept in a glovebox filled with argon gas and connected to a galvanostat outside the glovebox. A confocal microscope is applied to observe the cross-sectional view of the battery during battery operation. (E) Digital photos and schematics of the battery device for optical microscopy observation (upper panels); and sequential micrographs showing lithium being continuously electroplated onto the lithium electrode surface during accelerated electrochemical charging (lower panels). Reprinted from Harris, S.J., *et al.*, 2010. Direct in situ measurements of Li transport in Li-ion battery negative electrodes. *Chemical Physics Letters* 485 (4–6), 265–274. Available at: <https://doi.org/10.1016/j.cplett.2009.12.033>. Copyright (2010), with permission from Elsevier. Aryanfar, A., *et al.*, 2014. Quantifying the dependence of dead lithium losses on the cycling period in lithium metal batteries. *Physical Chemistry Chemical Physics* 16 (45), 24965–24970. Available at: <https://doi.org/10.1039/C4CP03590A>. Copyright 2014, Royal Society of Chemistry. Bai, P., *et al.*, 2016. Transition of lithium growth mechanisms in liquid electrolytes. *Energy & Environmental Science* 9. Copyright 2016, The Royal Society of Chemistry. Sun, M., *et al.*, 2021. Visualizing lithium dendrite formation within solid-state electrolytes. *ACS Energy Letters* 6 (2), 451–458. Available at: <https://doi.org/10.1021/acsenenergylett.0c02314>. Copyright 2021 American Chemical Society. Wu, H., *et al.*, 2014. Improving battery safety by early detection of internal shorting with a bifunctional separator. *Nature Communications* 5 (1), 5193. Available at: <https://doi.org/10.1038/ncomms6193>. Copyright (2014) permission from Springer Nature.

decomposition of the electrolyte. Using a similar experimental setup, Lang *et al.* captured the changes in the surface topography of HOPG electrode due to dynamic nucleation, growth, deposition, and dissolution of insoluble Li_2S_2 and Li_2S at the cathode/electrolyte interface in Li/LiPS semi-liquid batteries (Lang *et al.*, 2016). Fig. 9(B) shows the change in the surface morphology of the electrode during the CV scan. In the reduction process, Li_2S_8 converted first to Li_2S_2 as NP deposits then to the growth of Li_2S forming lamella structure. Upon oxidation, Li_2S lamella was decomposed from the sediment/electrode interface leaving the Li_2S_2 particles which accumulated during cycling leading to the irreversible capacity fading of LSBs.

In addition to analyzing the structural evolution, nano-indentation using a cantilever tip with a known force constant can evaluate the evolution of the microstructure and the mechanical property of the electrode during lithiation and delithiation.

McAllister *et al.* (2014) first introduced an in situ AFM nanoindentation technique to observe the change in the mechanical property of amorphous silicon nanopillar anode during the first lithiation and delithiation cycle. They discovered that the mechanical degradation/recovery of the pillars upon lithiation-delithiation cycle were affected by the pillar size with the intermediate-sized pillar showing the most significant recover, indicating that there is an optimum pillar diameter for maximum retention of the mechanical properties of Si nanopillar battery electrodes. Breitang *et al.* analyzed the surface topology of nano-silicon anodes containing polymer binder and carbon black conductive additives while electrochemical reactions were taking place in the cell, and the formation/evolution of the SEI layer was characterized by phase imaging and nano-indentation (Breitung *et al.*, 2016). As shown in Fig. 9(C), force-displacement curves from nano-indentation of lithiation Si NPs clearly show the initial penetration of the indenter through the ~ 45 nm thick soft SEI layer on the surface. Development and stabilization of the SEI layer was confirmed by phase imaging of the electrode surface showing transition from initial SEI development (granular structure indicating the variation in the hardness) to stable SEI (uniform contrast corresponding to a single phase with distinct hardness).

The limitation of AFM also applies to in situ AFM. For instance, the open cell configuration is necessary, hence a controlled inert environment is required. Image acquisition is a relatively slow process in AFM, and the surface structures may be modified during the scanning process. Also, it is only suitable for surface topography analysis and requires to be used with other in situ/operando techniques for bulk analysis.

X-ray

X-ray techniques are useful tools to study electrochemical reactions of energy materials providing information about their electronic and crystal/atomic structures (Bak *et al.*, 2018; Ghigna and Quartarone, 2021; Yang *et al.*, 2021). Commonly used in situ/operando X-ray techniques are XRD, XAS, XPS, and XCT. In situ XRD is used to study the change in the crystal structures of the electrode and electrolyte materials during charge/discharge cycles. In situ XAS provides element specific information on the evolution of local atomic arrangements and the electronic structures of the materials in battery cycles. Two distinct energy regions from XAS are used for the characterization: (1) XANES (within ~ 30 eV of the adsorption edge used to analyse electronic structures, oxidation states, and site symmetries) and EXAFS (above 40 eV extending to few hundred eV from the adsorption edge used to characterize structural information such as bond length, coordination number, and ordering/disordering). Modified coin-cell with X-ray transparent windows made of beryllium (Richard *et al.*, 1997), Kapton tape (Brant *et al.*, 2016), or thin polymer/metal films (Borkiewicz *et al.*, 2015), as shown in Fig. 10(A), are typically used in the experiments. Zhou *et al.* used in situ XRD and XAS (XANES) to discover intermediate phases induced by high-rate charging in the layered cathode for LIB (Zhou *et al.*, 2016). While typical phase transition of solid solution $\rightarrow$ two phase $\rightarrow$ solid solution, involving two hexagonal phases (H1 and H2) (Zheng *et al.*, 2019), is observed for low charge rate (0.1 C), a new, broad peak emerged between the H1 and H2 phases when the C rate is increased to 10 C, and becomes more pronounced at higher rates (Fig. 10(B), upper panel). This indicates the formation of intermediate phases. XANES data provides the change in the oxidation states. The K-edge of Ni shifted to the higher energy indicating the increase in the charge state from Ni^{2+} to Ni^{4+} during the charge process. However, Co and Mn exhibit no energy shift, which indicates these elements do not contribute much to the charge compensation. Ni K-edge shift as a function of SOC at different C rate shows that the oxidation state of Ni ions is higher at faster charging rates, especially at the intermediate SOC. The large overpotential at high C-rate provided extra driving force to overcome the energy barrier for the nucleation of the intermediate phases and facilitated the multiphase reactions contributing to the efficient Li extractions.

XPS is another powerful X-ray technique widely used to study battery materials, which provides atomistic and microscopic view of chemical speciation and distribution at complex electrode-electrolyte interfaces (Shutthanandan *et al.*, 2019). It is particularly useful in understanding the component of SEIs. In situ/operando XPS delivers real time view of SEI formation and development in the battery cycle contributing to understanding the failure mechanism. Nadasiri *et al.* employed in situ XPS using IL electrolyte to study the evolution of SEI on lithium metal in LSB (Nandasiri *et al.*, 2017), and captured elemental and chemical state distribution of SEI layer and their evolution at the Li metal anode after each cycle (Fig. 10(C)). Here, IL was used to withstand the UHV in the XPS chamber. XPS analysis is suitable for studying ASSB. Wood *et al.* (2018) observed a chemical transformation of LPS SSE into SEI phases at the interface with plated lithium, which was driven by Li^+ migration as shown in Fig. 10(D).

XCT constructs 3D images from a series of X-ray images of a sample taken from different angles. Synchrotron XCT has been used in situ/operando studies to capture 3D dynamic processes at nano-meter resolutions (Ebner *et al.*, 2013; Patterson *et al.*, 2016; Bak *et al.*, 2018; Lu *et al.*, 2020). For example, 3D morphological evolution of Zn dendrites in initial growth, dissolution/regrowth, and penetration through separator was captured by Yufit *et al.* (2019) as shown in Fig. 10(E). In situ XCT can be combined with XANES analysis to construct 5D data sets to track phase evolutions. Wang *et al.* (2016a) conducted in situ XANES nanotomography and established 3D features of a single-particle phase evolution for LiFePO_4 during charge and confirmed as shown in Fig. 10(F).

NMR

NMR is a useful non-invasive technique that allows analyses of all phases including crystalline, amorphous, liquid, and gaseous phases simultaneously and suitable for detecting on a working battery system (Blanc *et al.*, 2013; Hu *et al.*, 2018). It has been used to study various electrochemical reactions including phase changes, intermediate chemical reaction mechanism, cathode dissolution in electrolytes, and electrolyte degradation etc., over a wide range of temperature (Bhattacharyya *et al.*, 2010; Xiao *et al.*,

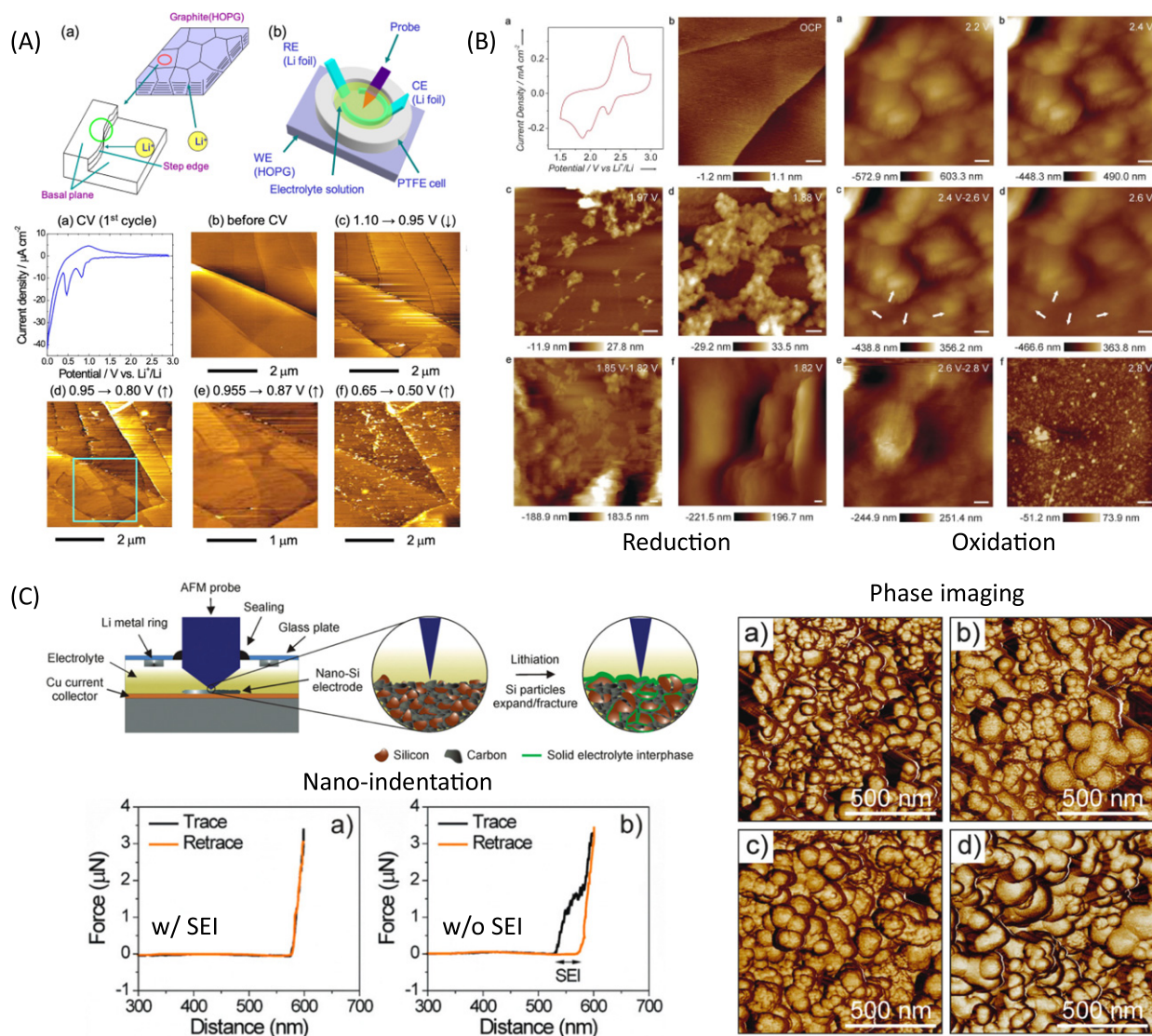


Fig. 9 (A) Schematic illustration of in situ AFM setup to observe surface of SEI formation on HOPG and AFM images of the HOPG basal plane surface obtained at different potentials during CV scan. (B) CV curve of the first cycle in a Li/LiPS cell and evolution of the surface topography of the HOPG at different potentials during reduction and oxidation. Scale bars are 100 nm and 1 μm for reduction and oxidation images, respectively. (C) In situ AFM combined with phase imaging and nano-indentation for analyzing SEI development in nano-silicon electrode. Schematic illustration of the experimental setup, nano-indentation force-distance profiles of lithiated silicon NPs with and without SEI, and phase imaging of nano-silicon electrode (a) before and after (b) 1, (c) 5, and (d) 10 cycles. Adapted with permission from Inaba, M., Jeong, S.-K., Ogumi, Z., 2011. In Situ scanning probe microscopy of interfacial phenomena in batteries. *The Electrochemical Society Interface* 20 (3), 55. Available at: <https://doi.org/10.1149/2.F05113if>. Copyright 2011 IOP Publishing, Ltd. Lang, S.-Y., *et al.*, 2016. Insight into the interfacial process and mechanism in lithium-sulfur batteries: An In Situ AFM study. *Angewandte Chemie International Edition* 55 (51), 15835–15839. Available at: <https://doi.org/10.1002/anie.201608730>. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Breitung, B., *et al.*, 2016. In situ and operando atomic force microscopy of high-capacity nano-silicon based electrodes for lithium-ion batteries. *Nanoscale* 8 (29), 14048–14056. Available at: <https://doi.org/10.1039/C6NR03575B>. Copyright 2016 Royal Society of Chemistry.

2015; Zhao *et al.*, 2020). To overcome a major challenge in in situ NMR of LIBs to separate resonances from different component, Li NMR is conducted using ^7Li instead of ^6Li due to its sensitivity (Trease *et al.*, 2011). Geral *et al.* was the first to employ ^7Li in situ NMR for studying the Li intercalation mechanism in different types of carbon-based materials and confirmed that it can detect the intercalated and dendritic lithium even with the presence of the lithium counter electrode (Gerald *et al.*, 2000).

A schematic of a typical NMR experimental setup for studying battery reactions is shown in Fig. 11(A). The analysis is performed for an entire battery using a coin-cell (Gerald *et al.*, 2000), flat plastic bag (Letellier *et al.*, 2007), or cylindrical cell designs (Poli *et al.*, 2011), which are placed in a NMR coil to record NMR spectra at different SOC. Since the collected signals are from the entire battery cell, separating contributions from the different components of the cell is not straight forward because of the overlapping resonances. Nevertheless, in situ NMR provides useful information on the electrochemical reaction mechanisms of batteries. Key *et al.* (2009) conducted in situ NMR to analyze the lithiation process of Si in Si/Li half-cell setup. As shown in Fig. 11(B), upon discharge, an

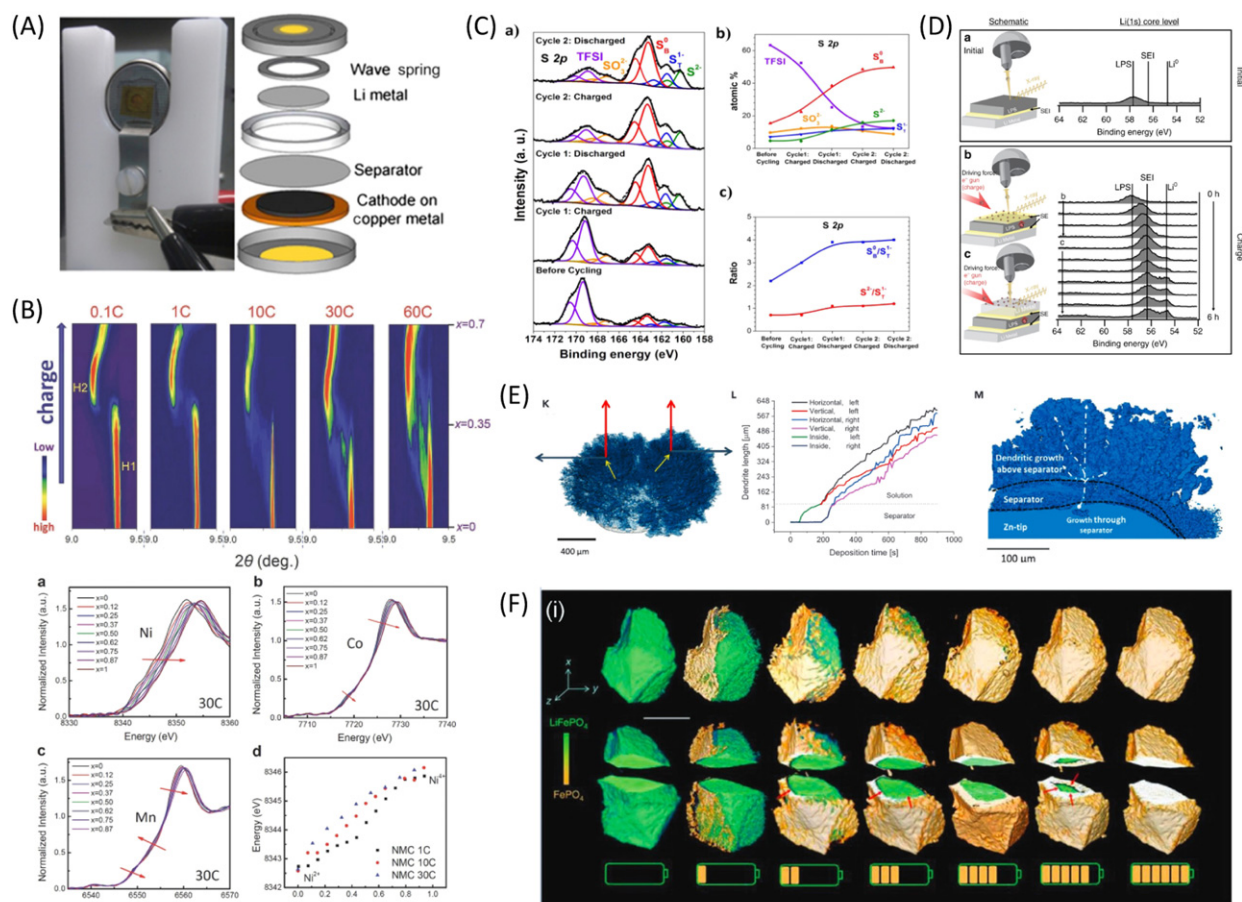


Fig. 10 (A) Modified coin-cell with Kapton window for X-ray experiments. (B) In situ XRD of NMC cathode at different charge rate showing contour plot of the (003) diffraction peak of $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with increasing x between $x = 0$ and 0.7 during the first charge process at different C rates (upper panel), shifts in XANES of (a) Ni, (b) Co, and (c) Mn K-edge during 30 C charge, and (d) Ni K-edge energy shift as a function of nominal lithium content x in NMC during initial charge process at the charge rates of 1 C, 10 C, and 30 C. (C) (a) Core level S 2p XPS spectra of the Li-electrolyte interfacial region with subsequent charge/discharge cycles, (b) evolution of various sulfur-based species over charge/discharge cycles based on atomic concentration derived from S 2p peak areas, and (c) the ratio between terminal sulfide and bridging sulfur atoms ($\text{S}_\text{B}^0/\text{S}_\text{T}^{1-}$) along with the disulfide and sulfide ratio ($\text{S}^{2-}/\text{S}^{1-}$) derived from S 2p peak areas. (D) Schematics and Li 1s core level shift of *In situ* XPS analysis of Li/LPS interface during charge. (E) In situ XCT observation of the evolving Zn dendrites during initial growth. Reconstructed 3D image of Zn dendrites from in situ XCT observation (left), dendrite growth profile on left and right sides of the zinc anode (middle), and a cross-sectional image of the dendrites that have perforated the separator after the initial growth (right). (F) In situ XANES nanotomography of a LiFePO_4 particle during charge. Reprinted from Brant, W.R., *et al.*, 2016. Comparative analysis of ex-situ and operando X-ray diffraction experiments for lithium insertion materials. *Journal of Power Sources* 302, 126–134. Available at: <https://doi.org/10.1016/j.jpowsour.2015.10.015>. With permission from Elsevier. Zhou, Y.-N., *et al.*, 2016. High-rate charging induced intermediate phases and structural changes of layer-structured cathode for lithium-ion batteries. *Advanced Energy Materials* 6 (21), 1600597. Available at: <https://doi.org/10.1002/aenm.201600597>. Copyright 2016 WILEY-VCH Verlag GmbH & Co. Nandasiri, M.I., *et al.*, 2017. In Situ chemical imaging of solid-electrolyte interphase layer evolution in Li-S batteries. *Chemistry of Materials* 29 (11), 4728–4737. Available at: <https://doi.org/10.1021/acs.chemmater.7b00374>. Copyright 2017 American Chemical Society. Wood, K.N., *et al.*, 2018. Operando X-ray photoelectron spectroscopy of solid electrolyte interphase formation and evolution in Li_2S -P2S₅ solid-state electrolytes. *Nature Communications* 9 (1), 2490. Available at: <https://doi.org/10.1038/s41467-018-04762-z>. With permission from Elsevier. Yufit, V., *et al.*, 2019. Operando visualization and multi-scale tomography studies of dendrite formation and dissolution in zinc batteries. *Joule* 3 (2), 485–502. Available at: <https://doi.org/10.1016/j.joule.2018.11.002>. Wang, J., *et al.*, 2016a. Visualization of anisotropic-isotropic phase transformation dynamics in battery electrode particles. *Nature Communications* 7 (1), 12372. Available at: <https://doi.org/10.1038/ncomms12372>. With CC BY.

emerging resonance at -10 ppm was observed, which was not seen by *ex situ* NMR analysis. The -10 ppm resonance was from a highly reactive metastable $\text{Li}_{15+\delta}\text{Si}_4$, that “self-charges” (self-discharge when pairing Si with cathode such as LiCoO_2) leading to the loss of Li from this phase.

Because of the difference in the size, resonances from bulk and dendritic (mossy) Li can be separated. The penetration of RF fields used to excite nuclear transitions in NMR is severely limited through metal samples, an effect known as skin depth. Since the thickness of the dendritic lithium is an order of magnitude smaller than the skin depth, RF signal fully penetrates the dendrites. Bhattacharyya *et al.* (2010) used this phenomena to separate resonances from dendritic lithium and smoothly deposited bulk lithium and quantified the effect of electrolyte and current density on the formation of dendrites as shown in Fig. 12(C). Similarly,

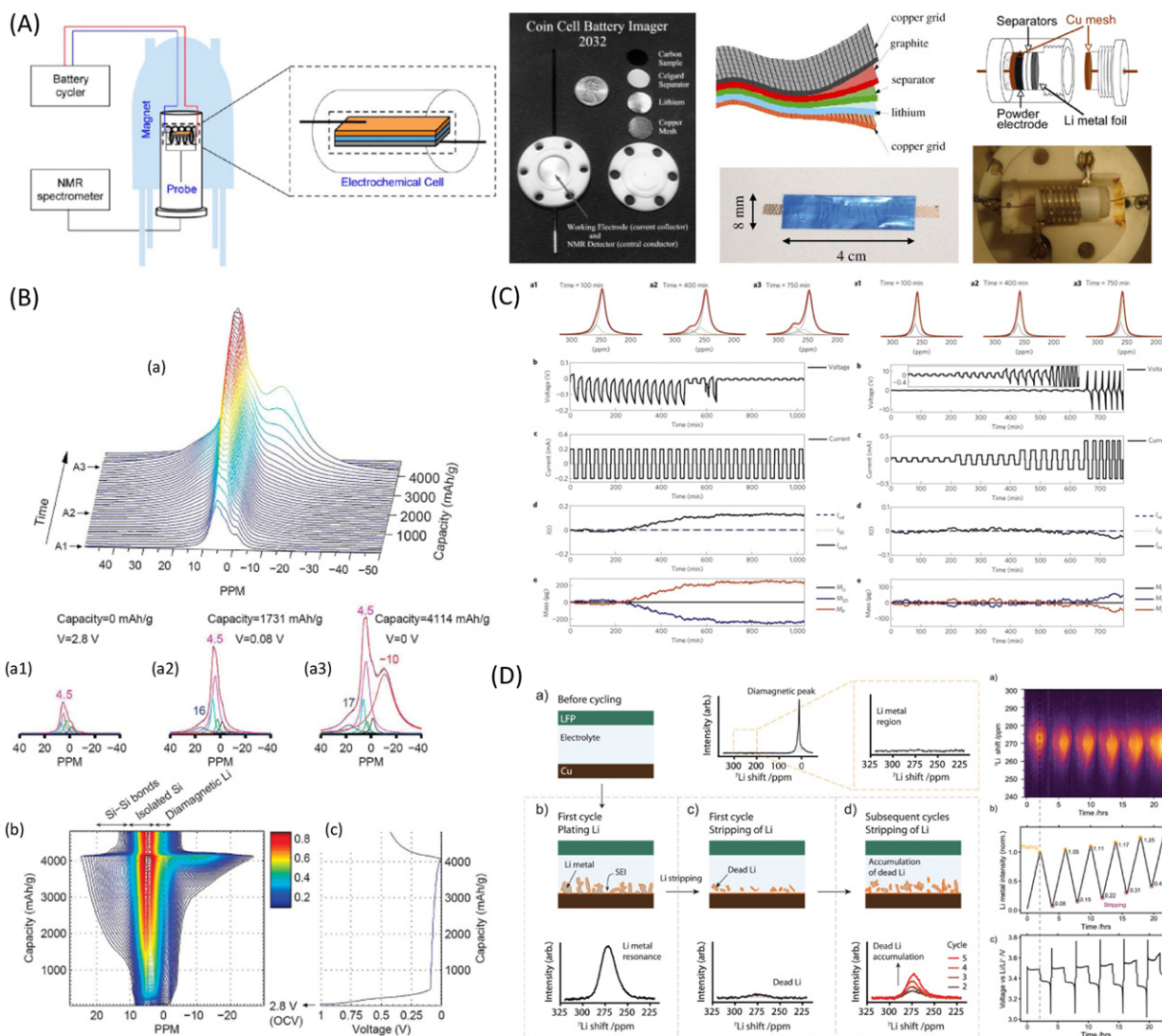


Fig. 11 (A) Schematic illustrating of in situ NMR setup. Examples of coin-cell, plastic bag, and cylindrical cell designs are shown. (B) Stacked(a) and contour(b) plots of in situ ^7Li static NMR spectra and electrochemical profile of the first discharge (c) of an actual crystalline Si vs Li/Li^+ battery (the color bar shows the relative intensity scale for the spectra). (a1) – (a3) are deconvoluted spectra at various discharge capacity values of interest. (C) The effect of multiple charge–discharge cycles on the ^7Li NMR spectra of a metallic lithium symmetric cell containing an ionic–liquid electrolyte ($\text{C}_2\text{mim BF}_4 + \text{LiBF}_4$) and a VC additive (left) and $\text{C}_4\text{mpyr}-\text{TFSI} + \text{LiTFSI}$ (right). (D) Accumulation of dead lithium quantified by in situ NMR of anode-free Cu-LFP battery. Images reproduced with permission from Blanc, F., Leskes, M., Grey, C.P., 2013. In Situ solid-state nmr spectroscopy of electrochemical cells: Batteries, supercapacitors, and fuel cells. *Accounts of Chemical Research* 46 (9), 1952–1963. Available at: <https://doi.org/10.1021/ar400022u>. Copyright 2013 American Chemical Society. Letellier, M., Chevallier, F., Morcrette, M., 2007. In situ ^7Li nuclear magnetic resonance observation of the electrochemical intercalation of lithium in graphite; 1st cycle. *Carbon* 45 (5), 1025–1034. Available at: <https://doi.org/10.1016/j.carbon.2006.12.018>. Gerald, R.E., *et al.*, 2000. ^7Li NMR study of intercalated lithium in curved carbon lattices. *Journal of Power Sources* 89 (2), 237–243. Available at: [https://doi.org/10.1016/S0378-7753\(00\)00435-3](https://doi.org/10.1016/S0378-7753(00)00435-3). Poli, F., *et al.*, 2011. New cell design for in-situ NMR studies of lithium-ion batteries. *Electrochemistry Communications* 13 (12), 1293–1295. Available at: <https://doi.org/10.1016/j.elecom.2011.07.019>. Key, B., *et al.*, 2009. Real-Time NMR investigations of structural changes in silicon electrodes for lithium-ion batteries. *Journal of the American Chemical Society* 131 (26), 9239–9249. Available at: <https://doi.org/10.1021/ja8086278>. Bhattacharyya, R., *et al.*, 2010. In situ NMR observation of the formation of metallic lithium microstructures in lithium batteries. *Nature Materials* 9 (6), 504–510. Available at: <https://doi.org/10.1038/nmat2764>. Gunnarsdóttir, A.B., *et al.*, 2020. Noninvasive In Situ NMR study of “Dead Lithium” formation and lithium corrosion in full-cell lithium metal batteries. *Journal of the American Chemical Society* 142 (49), 20814–20827. Available at: <https://doi.org/10.1021/jacs.0c10258>.

Gunnarsdóttir *et al.* (2020) developed an in situ NMR technique to quantify dead lithium in anode-free Cu-LFP battery to determine the origin of lithium losses and the degradation mechanism. As shown in Fig. 11(D), accumulation of dead lithium was successfully quantified during the charge/discharge cycles. Using this technique, the multiple capacity losses that occur in lithium metal batteries were deconvoluted, and the effect of electrolytes as well as the compatibility of protective coatings and artificial SEIs for Li deposition were further studied.

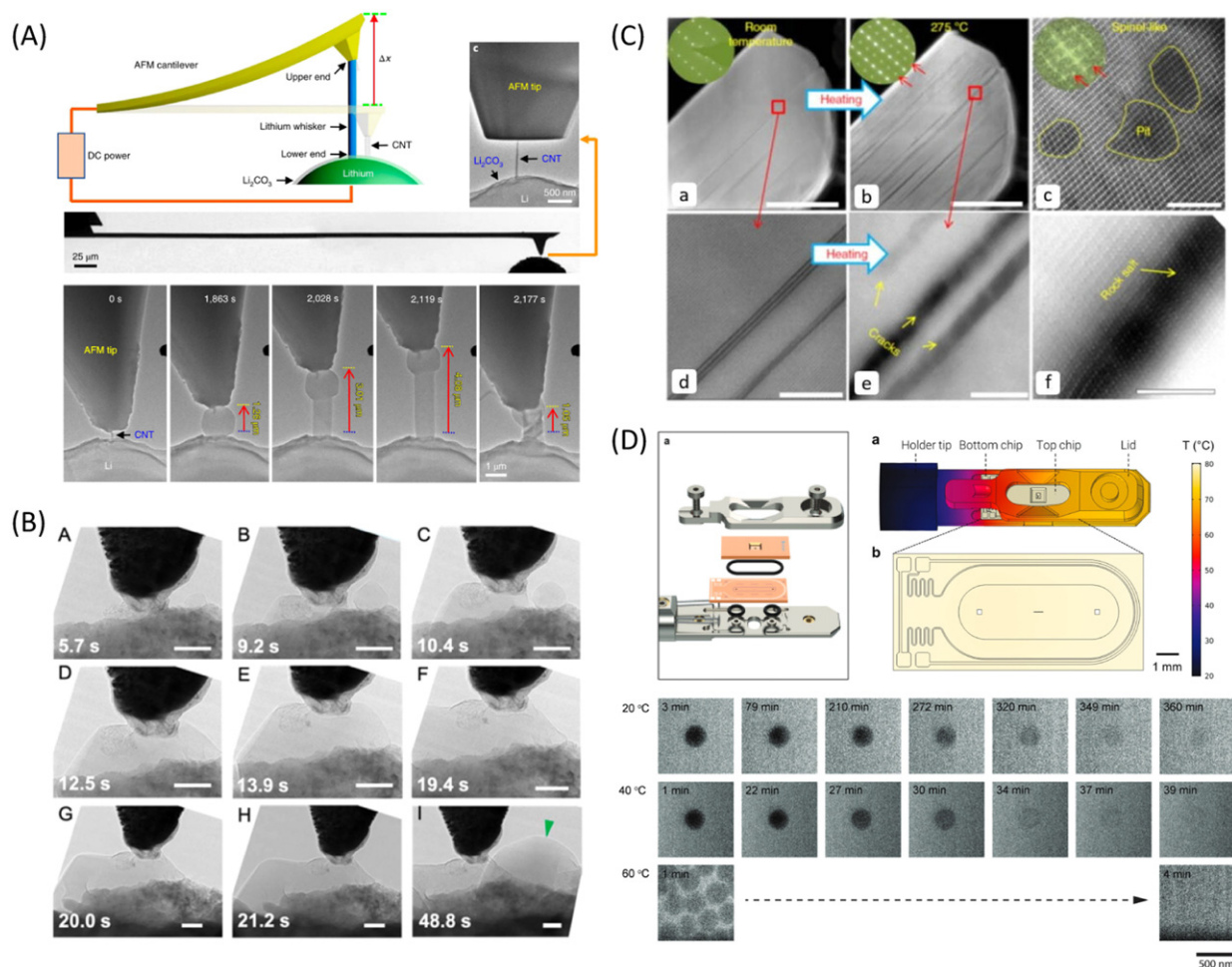


Fig. 12 (A) Schematic of the AFM-TEM set-up used for observation and measurement of Li whisker growth. An arc-discharged CNT was attached to a conducting AFM tip by electron beam deposition of carbonaceous materials, and this assembly was used as a cathode; the scratched Li metal on the top of a sharp tungsten needle was used as an anode; and the naturally formed Li₂CO₃ on the Li surface was used as a solid electrolyte. Time-lapse TEM images of Li whisker growth show a nano-sized Li ball nucleated from the CNT and started to grow into a whisker emerging underneath the ball, which pushed the AFM cantilever up, thus generating the axially compressive stress in the whisker. (B) Electrochemical plating of lithium and quantification of the growth force. The growth direction switched from vertical to parallel with respect to the SSE surface after the compressive force between the cantilever tip and the lithium reached the threshold. (C) *In situ* heating-induced crack nucleation and propagation. The LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622) was delithiated by charging to 4.7 V vs. Li metal. (a) and (b) HAADF images from delithiated NMC622 before heating (RT). c–f HAADF images after heating to 275 °C. SAED patterns and FFT images in (a), (c), and (e) show the overall lattice change during heating. d, e, and f show local lattice structure change at crack regions and crack-free regions. The scale bars are 200 nm in (a) and (c); 10 nm in (b) and (d); and 4 nm in (e) and (f). (D) Schematic illustration of liquid-cell with a heating element and the predicted temperature distribution by FEA (upper panel), and temperature dependent etching kinetics of silica nanoparticles (lower panel). Reprinted by permission from Zhang, L., *et al.*, 2020b. Lithium whisker growth and stress generation in an in situ atomic force microscope–environmental transmission electron microscope set-up. *Nature Nanotechnology* 15 (2), 94–98. Available at: <https://doi.org/10.1038/s41565-019-0604-x>. Diaz, M., Kushima, A., 2021. Direct observation and quantitative analysis of lithium dendrite growth by In Situ transmission electron microscopy. *Journal of The Electrochemical Society* 168 (2), 020535. Available at: <https://doi.org/10.1149/1945-7111/abe5ec>. Yan, P., *et al.*, 2018. Coupling of electrochemically triggered thermal and mechanical effects to aggravate failure in a layered cathode. *Nature Communications* 9 (1), 2437. Available at: <https://doi.org/10.1038/s41467-018-04862-w>. van Omme, J.T., *et al.*, 2020. Liquid phase transmission electron microscopy with flow and temperature control. *Journal of Materials Chemistry C* 8 (31), 10781–10790. Available at: <https://doi.org/10.1039/D0TC01103G>.

Future Perspectives

The past few decades have witnessed introduction and development of various in situ/operando techniques for studying energy materials. They have been making significant contributions to the advancement of the energy technologies by providing fundamental insights into understandings of the dynamic processes at different temporal and spatial scales. As explained above, each technique has its own advantages and limitations mainly due to the constraints from the required experimental setups for the instrument such as sample size/geometries, temperatures, atmospheric/vacuum condition, special/temporal resolutions, etc. At the early introduction and development stages of the in situ/operando techniques, observation of phenomena “for the first time” would provide useful information toward understanding the materials properties and dynamic processes, even when the

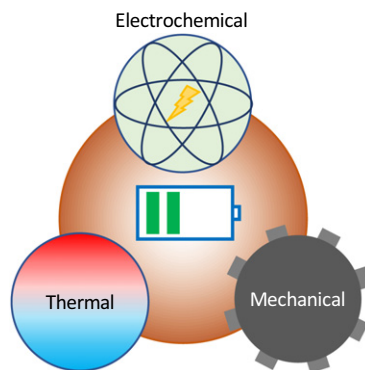


Fig. 13 Schematic illustration of the future direction for developing advanced in situ/operando characterization techniques.

experiments were performed at the required conditions of the instruments different from those inside the actual devices. Now that the in situ/operando techniques have gained much popularity and became widely accepted tools that play an important role in the research and development of the energy technologies, there is a growing demand to perform these in situ/operando experiments at the conditions same as or close to the real working environment of the systems. This led to the development of the in situ closed-cell TEM to study electrochemical reactions in the batteries using actual electrolytes that can evaporate inside the TEM, for example.

In energy storage devices, there are complex interactions between electrochemical, thermal, and mechanical processes, and evaluating their links is important for understanding the fundamental properties of the devices to provide novel design or plan to improve the performance or mitigate the failures. For instance, failures of ASSLIB are caused by the penetration of lithium in the SSE. Recently, Zhang *et al.* combined AFM probe with in situ TEM to study the growth force of lithium dendrites from SSE (Fig. 12(A)) (Zhang *et al.*, 2020b, p. 1). Diaz *et al.* employed a similar technique and evaluated the threshold stress to change the lithium growth direction from vertical to parallel direction with respect to the SSE surface at the initial nucleation and growth stage (Fig. 12(B)) (Diaz and Kushima, 2021). These methods enable direct observations and quantifications of the mechanical stress and response arising from the electrochemical plating of lithium.

Effect of temperature in the battery performance is another important field of study. Kaboli *et al.* (2020) performed in situ SEM under elevated temperature to study the evolution of the passivation layer between Li and SSE. Yan *et al.* (2018) performed in situ heating experiments inside a TEM and discovered an atomic-scale mechanism of thermal cracking of NMC particles associated with electrochemically induced phase inhomogeneity and internal pressure resulting from oxygen release (Fig. 12(C)). The heating experiments in SEM/TEM are typically performed in open-cell setup. However, a heating element can be integrated in a liquid-confining cell to study the reactions under elevated temperature (Fig. 12(D)) (Omme *et al.*, 2020). Therefore, in situ liquid-cell TEM can be performed to study the electrochemical reactions under elevated temperature. On the other hand, the loss of performance and the degradation of LIBs under extreme low temperature has been a major issue for EVs used in arctic climates (Hu *et al.*, 2020). Evaluating the effect of low temperature on the atomic/nano-scale electrochemical reaction may offer fundamental understanding of the degradation mechanism to overcome these issues. To date, there is no liquid-cell TEM that can conduct experiment under low temperature, which leaves significant scope for further improvement.

In situ/operando characterization technique has become an essential tool for material and device R&Ds for energy storage technologies. However, there are still room for further improvement. The development is expected to continue toward enabling the reproduction of the actual device working condition and quantifying multi-physical interactions between electrochemistry, thermodynamics, and mechanics (Fig. 13). There are many challenges to be overcome. However, pioneering works to bring forth novel methods and/or instruments for advanced in situ/operando characterization technique will extend its map into new material properties and dynamic phenomena to be explored, contributing to the further development of the technology.

Conclusions

This article compiled variety of in situ/operando techniques used to study fundamental science of electrochemical reactions in energy materials. Characteristics of different methods were explained along with representative examples of their applications. The current limitations and future opportunities of the advanced characterization techniques were also discussed. On the other hand, there are many review papers focusing on individual techniques introduced in this article, and further reading of such articles is recommended to gain more in-depth understandings of the methods and their implementation in the energy research as listed below.

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In recent years considerable advances have taken place in materials in general and in Electronics materials in particular. Developments have taken place in their applications and processing technologies. The pace of new developments and applications is progressing at an accelerated rate. It is therefore vitally important that researchers, academics, design engineers, and manufacturing technologists be up to date with these new developments. Such developments open up excellent opportunities to improve effective utilization of material resources, improve efficiency, reliability, durability, and cost effectiveness of the products. These developments should serve researchers all over the world in keeping them fully abreast of such new applications.

The Encyclopedia of Materials: Electronics is a one-stop resource consolidating and enhancing the literature of the Electronic materials. This Section of the Encyclopedia addresses recent progress in Electronic materials, particularly nanomaterials and their applications as well as covering recent developments in specific materials for applications in engineering, biomedical, environmental protection, health and safety, and sensor materials and their developments. The exposure of these aspects will assist scientists and engineers in the selection, design, and usage of sensor materials in newer practical applications.

As the editor of this Section of the Encyclopedia I am greatly indebted to the contributors who are experts in their respective fields, for their topics for their articles. Their true dedication to the scientific community is reflected in the time and energy they have given to this Section of the Encyclopedia. Their insight and specialist knowledge in their respective articles is reflected in the high quality of this work. Myself along with other section editors are greatly appreciative of all the hard work undertaken by the Editor-in-Chief, Professor A.S.M.A. Haseeb to turn this idea into a publishable work. Our special thanks go to Rekha Nimesh, the project manager, along with the rest of the team at Elsevier who served successively to keep the project on track through friendly nudges in order to ensure timely completion.

The extensive academic discussion of core theories and applications, supplemented by applied case studies and advanced multimedia features has drawn together numerous areas of research and I sincerely hope that the work of this Section will prove to be of great help to both the young and experienced members of the international research community, academics, and industrial practitioners for years to come.

Synthesis of One Dimensional Nanostructures of TiO₂ by Thermal Oxidation

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Introduction

Metal oxides are interesting materials which can exhibit metallic, semiconducting, or insulating characteristics. A wide variety of engineering applications uses metal oxides such as ZnO, SnO₂, TiO₂, In₂O₃, WO₃, TeO₂, CuO, CdO, Fe₂O₃, and MoO₃. Out of these, TiO₂ gained great attention for its use in solar cells, gas sensors, white pigments, corrosion protective coating, optical coating, ceramics, electrical devices, bone implants, and catalyst (Diebold, 2003). High temperature stability, superior chemical stability, corrosion protective properties, improved hardness, and higher band gap make TiO₂ particularly suitable for these engineering applications. Combining TiO₂ with other metal oxides may result in composite oxides with novel properties suitable for specific applications. For example, nanocomposite film consisting of TiO₂ and Al₂O₃ are being used as passivation layer in electronic devices (Kim *et al.*, 2014b), gas sensors (Lü *et al.*, 2013; Karaduman *et al.*, 2015), capacitors (Liun *et al.*, 2014; Zhang *et al.*, 2014a), photo-catalysts (Chu *et al.*, 2005, 2003), solar cells (Kim *et al.*, 2014a), anti-reflection coatings and optical filters (Mitchell *et al.*, 2006) for their superior properties over single phase TiO₂. Nanocomposite structures consisting of TiO₂-C are being used in lithium ion batteries (Park *et al.*, 2011a,b; Xia *et al.*, 2014; Zhang *et al.*, 2014b), photo-catalyst (Tsumura *et al.*, 2002), and super capacitor (Zheng *et al.*, 2013). Different forms of these composite structures such as nanocomposite layers/films (Karaduman *et al.*, 2015; Liun *et al.*, 2014; Aner and Tepehan, 2014; Mohammadi, 2014), nanolaminate (Kim *et al.*, 2014b; Mitchell *et al.*, 2006; Zhang *et al.*, 2014a), nanoparticles (Arafat *et al.*, 2014), one dimensional (1-D) nanostructures (Lü *et al.*, 2013; Ku *et al.*, 2013), and core-shell structures (Park *et al.*, 2011b) have been investigated for different applications. Recent studies have shown that high surface to volume ratio is desirable in many applications of single phase and nanocomposite TiO₂. For this reason, different nanostructures of TiO₂ including 1-D with different morphologies have been tested in applications such as gas sensors (Varghese *et al.*, 2003; Francioso *et al.*, 2008), super capacitors (Zheng *et al.*, 2013), lithium ion batteries (Park *et al.*, 2011b), and solar cells (Kim *et al.*, 2014a).

The production of 1-D TiO₂ nanostructures can be accomplished by highly sophisticated procedures such as hydrothermal (Zhang *et al.*, 2002; Shim *et al.*, 2010), electrospinning (Lee *et al.*, 2011; Archana *et al.*, 2009), anodization (Wang *et al.*, 2009; Wang and Lin, 2008), UV lithography (Francioso and Siciliano, 2006; Francioso *et al.*, 2008), and atomic layer depositions (Lotfabad *et al.*, 2013). Obtaining nanocomposite structures based on 1-D TiO₂ requires manipulation and/or combination of two or more processes which is complex, time consuming, and expensive. Recently, it has been shown that 1-D nanostructures of TiO₂ can be synthesized by a simple, inexpensive, highly scalable process named thermal oxidation. This process requires heating Ti substrates under low oxygen containing environments (10 s of ppm O₂ in some inert atmosphere). Furthermore, nanocomposite core-shell TiO₂-Al₂O₃ structure can be obtained by choosing Ti alloy substrates containing Al such as Ti-6Al-4V (Ti64) (Arafat *et al.*, 2015). On the other hand, core-shell TiO₂-C structures were obtained by using oxygen containing hydrocarbons such as acetone (CH₃COCH₃) as an oxidation medium (Huo *et al.*, 2008, 2009). Thermal oxidation process is also capable to grow 1-D nanostructures on other metal substrates including copper (Cu) (Jiang *et al.*, 2002; Lin *et al.*, 2004), iron (Fe) (Fu *et al.*, 2003; Wen *et al.*, 2005), niobium (Nb) (Lima and Choi, 2009), tungsten (W) (Gu *et al.*, 2002), and zinc (Zn) (Ren *et al.*, 2007).

In this review article the thermal oxidation process of Ti and its alloy substrates is summarized for the production of 1-D nanostructures. The effects of the processing parameters such as alloying elements, microstructures of the substrates, oxidation environment, temperature, oxidation time, and residual stress are discussed in details. The characteristics of the as-grown nanostructures are discussed and correlated with the process parameters. Finally, the probable growth mechanism of the 1-D nanostructures on Ti and its alloy substrate has been outlined.

Nomenclature of the As-Grown Nanostructures

The as-grown nanostructures on Ti and its alloy substrates by thermal oxidation possess diameter and length in the range of 15–200 nm and 1–5 µm, respectively (Huo *et al.*, 2008; Peng and Chen, 2004; Arafat *et al.*, 2015). Nanostructures with different shape and morphologies are produced during the oxidation process. For this reason, different terminologies such as nanowires, nanorods, and nanofibers are used in the literature to describe the nanostructures. However, to avoid confusion, one dimensional (1-D) nanostructures is explicitly used in this article to denote different morphologies on Ti and its alloy substrate produced by thermal oxidation. However, the original terminologies reported in the literature are preserved in Table 1.

Thermal Oxidation Process

Thermal oxidation of Ti and its alloy substrates for the growth of 1-D nanostructures requires low levels of oxygen (10 s of ppm) in an inert gas, typically argon (Ar). The oxidation is carried out in a tube furnace system which is particularly designed for the 1-D growth on Ti and its alloy substrate as depicted in Fig. 1.

Table 1 Summary of the 1-D nanostructure grown by thermal oxidation process on Ti and Ti alloy substrates

Nanostructure	Substrate, dimensions, and source	Oxidation environment	Other conditions	Growth temperature (°C)	Growth time	Dimension of the 1-D nanostructures	Crystal structure	Growth direction	Reference
TiO ₂ nanowires	Ti foil(Aldrich, 99.7%), dimension: 10 mm×10 mm×1 mm	Acetone vapor in Ar	Flow rate: 50 sccm Post annealing in air at 650°C for 30 min is required to remove carbon from the shell.	800°C	1 h	Diameter: 20–50 nm	Rutile	–	(Huo et al., 2009)
TiO ₂ film	Ti plate (Grade1), dimension: 30 mm×15 mm×0.8 mm	Pure oxygen (99%)	Flow rate: 200 sccm	850°C	1.5 h	–	Rutile	–	(Peng and Chen,2004; Peng et al., 2005)
TiO ₂ nanofibers	Ti plate (Grade1), dimension: 30 mm×15 mm×0.8 mm	Mixture of Ar and O ₂	Flow rate:200 sccm(Ar)and 1 sccm (O ₂)	850°C	1.5 h	Chain-like structure: Diameter: 200 nm Length: several micrometers Ribbon-like structure: Width: 200–1500 nm Thickness: 60 nm Length: several micrometers	Rutile		(Peng and Chen, 2004)
TiO ₂ nanorods	Ti plate (Grade1),dimension: 30 mm×15 mm×0.8 mm	Acetone vapor in Ar	Flow rate: 200 sccm	850°C	1.5 h	Tetragonal structure: Width: ~1.5 μm Thickness: 100 nm Length: 1–2 μm Columnar structure: Diameter: 230 nm Length: 2–3 μm	Rutile	[0 0 1]	(Peng and Chen, 2004; Peng et al., 2005)
TiO ₂ micro-crystalline fibers	Ti plate(Grade1),dimension: 30 mm×15 mm×0.8 mm	Water vapor in Ar	Flow rate: 200 sccm	850°C	1.5 h	Diameter: ~1 μm Length: 5 μm	Rutile	–	(Peng et al., 2005)
TiO ₂ plate-like nanostrcutres	Ti plate (Grade1), dimension: 30 mm×15 mm×0.8 mm	Ethanol vapor in Ar	Flow rate: 200 sccm	850°C	1.5 h	Width: 500 nm Thickness: 150nm Length: 1 μm	Rutile	–	(Peng et al., 2005)
TiO ₂ nanorods	Tiplate(Grade1),dimension: 30 mm×15 mm×0.8 mm	Acetaldehyde vapor in Ar	Flow rate: 200 sccm	850°C	1.5 h	Width: 500 nm Thickness: 150nm Length: 1 μm	Rutile	–	(Peng et al., 2005)
TiO ₂ nanowire	Ti particles (H.C. Starck GmbH, Germany)	Ethanol	Pressure: 10 Torr	650–800°C	30–180 min	Diameter: 60–150 nm Length: ~2 μm	Rutile	–	(Kaewsai et al., 2010)
TiO ₂ nanowire	Ti wire (Advent Research Materials Ltd., 99.8%), diameter: 0.25 mm	Ethanol	Pressure: 10 Torr	650–800°C	30–180 min	Diameter: 23–73 nm	Rutile	[0 0 1]	(Daothong et al., 2007)
TiO ₂ nanorods	Ti plate (Grade1),dimension: 30 mm×15 mm×0.8 mm	Dibutyltin dilau- rate in Ar	–	600–900°C	4 h	Width: 150 nm Length: several hundred nanometer Height: 1.5 μm	Rutile	[0 0 1]	(Peng and Chen, 2005)

TiO ₂ nanowire	α-Ti bar (grade2)	Tens of ppm O ₂ Flow rate: 200 sccm in Ar	600°C	8 h	Length:50–400 nm	–	–	(Lee et al., 2010)
TiO ₂ nanowire	Ti64 coupon(Ti-6 Al-4V, Online metals, Seattle,WA, grade5)	Tens of ppm O ₂ Flow rate: 200–1000 sccm in Ar	700°C	8 h	–	–	–	(Lee et al., 2010)
TiO ₂ nanowire	β-Ti (5–5–5) bar(Ti-5Al-5V- 5Mo-3.5Cr-0.5Fe)	Tens of ppm O ₂ Flow rate: 200–1000 sccm in Ar	700°C	8 h	–	–	–	(Lee et al., 2010)
Core-shell TiO ₂ - Al ₂ O ₃	Ti64 coupon (Ti-6Al-4V, Online metals, Seattle,WA, grade5), dimension: 1 cm×1 cm	5–500 ppm O ₂ Flow rate: 500 sccm in Ar	700°C	8 h	Diameter: ~50–100 nm Length: 300nm–2 μm	Rutile	[0 0 1]	(Dinan et al., 2013)
Core-shell TiO ₂ - Al ₂ O ₃	Ti64 particles (Ti-6Al-4V, Powder Alloy Corporation, USA),size: 15.15–226.4 μm	20–80 ppm O ₂ Flow rate: 500 sccm in Ar	750°C	8 h	Diameter:20–40 nm Length: 2–3 μm	Rutile	–	(Arafat et al., 2013)
Core-shell TiO ₂ - Al ₂ O ₃	Ti64 particles (Ti-6Al-4V, Powder Alloy Corporation, USA),size: 15.15–226.4 μm	15 ppm O ₂ in ArFlow rate: 500 sccm	750°C	8 h	Diameter:30–100 nm Length: 1–5 μm	Rutile	–	(Arafat et al., 2015)
Core-shell TiO ₂ -C	Ti foil (99.6%),dimension: 10 mm×10 mm×1 mm	Acetone vapor inFlow rate: 150 sccm Ar	850°C	1.5 h	Diameter:15–20 nm (TiO ₂) Rutile		[1 0 1]	(Huo et al., 2008)

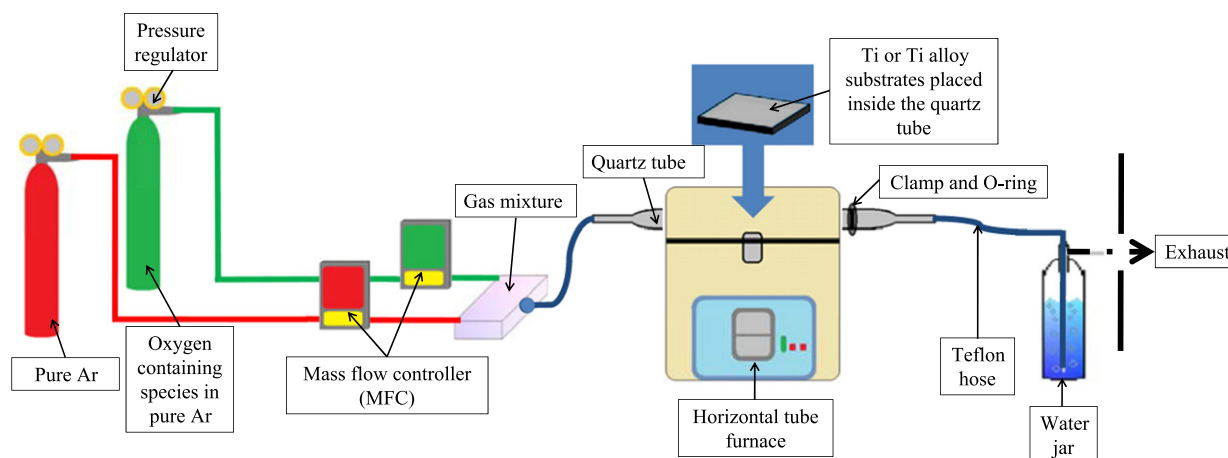


Fig. 1 Schematic experimental setup for the synthesis of 1-D nanostructures on Ti and its alloy substrate by thermal oxidation process. This figure is not to the scale.

The experimental system contains a quartz tube placed inside a furnace. The Ti or its alloy substrates are placed inside the quartz tube and sealed so that no gas from the ambient can enter inside during the oxidation process. One end of the quartz tube is connected to a gas mixture followed by mass flow controllers (MFCs) to control the flow rate of gases from the gas cylinders. Typically two cylinders are used for the oxidation of Ti and its alloy substrates for 1-D growth. One cylinder contains pure Ar gas whereas another cylinder composed of mixed gases containing oxygen (O_2) or oxygen containing species such as water (H_2O), acetone (CH_3COCH_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), acetaldehyde (CH_3CHO), formic acid (HCOOH), and dibutyltin dilaurate ($\text{C}_{32}\text{H}_{64}\text{O}_4\text{Sn}$) in Ar as tabulated in [Table 1](#). The concentration of oxygen or oxygen containing species in Ar varied in the range 10–1000 ppm. The gases from these cylinders are flown through the MFCs at different ratios to further dilute the oxygen or oxygen containing species in quartz tube during the oxidation process. The furnace is heated to the oxidation temperatures (600–900°C) and the substrate is allowed to react with the oxygen containing species for a certain period of time (30 min–8 h). During the oxidation process the gases are continuously flown and allowed to exhaust from the other end of the quartz tube. Finally, after oxidation for a certain period of time the furnace is cooled down to the room temperature and substrate is taken out for morphological investigations.

In another modification of tube furnace, only one cylinder containing pure Ar is used for the oxidation process. In that case, a bottle having oxygen containing species such as (water, acetone, and dibutyltin dilaurate) is placed and connected between MFCs and quartz tube ([Peng and Chen, 2004, 2005](#)). Ar from the cylinder is flown through the oxygen containing species inside the bottle. The oxygen containing species is carried to the quartz tube by the Ar carrier during oxidation. In some cases, the quartz tube is evacuated by a rotary pump to maintain a specific pressure during the oxidation process ([Daothong et al., 2007](#); [Kaewsai et al., 2010](#)). For the measurements of oxygen partial pressure and humidity inside the tube, oxygen and humidity sensors are used respectively in some modifications ([Lee et al., 2010](#)).

Variation of Metal Substrates for Thermal Oxidation

1-D nanostructures can be grown on a variety of Ti substrates by thermal oxidation process. During oxidation the nanostructures grow on the oxidized surface of the substrates. Ti foil/plates ([Huo et al., 2008, 2009](#); [Peng and Chen, 2004, 2005](#); [Peng et al., 2005](#)), bar ([Lee et al., 2010](#)), particles ([Kaewsai et al., 2010](#)), and wire ([Daothong et al., 2007](#)) showed acceptable amount of 1-D nanostructures during the thermal oxidation. Besides this, Ti alloy substrates such as Ti-6Al-4V (Ti64) plates ([Arafat et al., 2013](#)), Ti64 particles ([Arafat et al., 2013, 2015](#)), Ti64 bar ([Lee et al., 2010](#)), Ti-5Al-5V-5Mo-3.5Cr-0.5Fe (also known as β -Ti (5–5–5)) bar ([Lee et al., 2010](#)), and Ti-6.85Al-1.6V substrate ([Lee et al., 2010](#)) also showed high coverage of 1-D nanostructures during the oxidation process. So, it can be concluded that 1-D nanostructures can be grown on any shape of substrates of Ti and its alloys.

Effects of Oxidation Parameters

The synthesis process of 1-D nanostructures on Ti and its alloy is a substrate is very sensitive toward different parameters such as alloying elements, microstructures of the substrates, oxidation environment, temperature, oxidation time, and residual stress. Under different oxidation conditions nanostructures with different morphologies were formed which is tabulated in [Table 1](#). The effects of different parameters during thermal oxidation are discussed in the following sections.

Effects of Alloying Elements and Microstructures of Substrates

Significant amount of work for the synthesis of 1-D nanostructures by thermal oxidation was conducted on α -Ti substrates. However, it was found that the growth window for synthesizing 1-D nanostructures on α -Ti substrates is too narrow and requires a very low concentration of oxygen in Ar environment. Higher concentration of oxygen resulted in oxide scale instead of 1-D nanostructure. Moreover, the resultant nanostructures are not properly aligned with uniform thickness. The presence of the β phase stabilizers such as V, Mo, and Cr in the Ti matrix widens the window for the synthesis process of 1-D nanostructures with higher coverage (Lee *et al.*, 2010). Usually, Ti64 and β -Ti (5–5–5) contains a mixture of α and β phases in the microstructure. These alloys are found to be more suitable for the growth of 1-D nanostructures compared with α -Ti substrates (Lee *et al.*, 2010). As an example, for pure α -Ti substrates, the growth of 1-D nanostructures was found only in the presence of a minute amount of oxygen in Ar at a flow rate of 200 sccm (Peng and Chen, 2004; Lee *et al.*, 2010). On the other hand, for Ti64 and β -Ti (5–5–5) substrates, 1-D nanostructures can be grown at flow rates as high as 1000 sccm or more (Lee *et al.*, 2010). To further demonstrate the effect of alloy microstructure due to the presence of alloying elements, Ti-6.85Al-1.6V substrate (contained both α and β phase of Ti) was thermally oxidized at 700 °C for 8 h at a flow rate of 500 sccm (Lee *et al.*, 2010). Results revealed that the length and coverage of 1-D nanostructures are higher at the locations containing the β phase as shown in Fig. 2. α phase of Ti also showed growth of 1-D nanostructures but with less coverage and of shorter length. Thus the presence of β phase stabilizers such as V, Mo, and Cr in Ti matrix as alloying elements is particularly suitable for having higher coverage of 1-D nanostructures during thermal oxidation.

Effects of Oxidation Environment

Pure Ti is very sensitive toward the concentration of O₂ during the thermal oxidation process and require minute amount of O₂ for the growth of 1-D nanostructures. Excessive amount of O₂ results in the formation of oxide scale instead of 1-D nanostructures. Unlike the oxidation process for the growth of 1-D nanostructure on Cu and Fe substrates, pure O₂ and air are not suitable for the growth of 1-D nanostructures on Ti substrates. Peng and Chen (2004) and Peng *et al.* (2005) showed that oxidation of Ti in pure O₂ (99%) produced polycrystalline TiO₂ films instead of 1-D nanostructures as shown in Fig. 3(a). Similar results were obtained for the higher concentration of formic acid (HCOOH) as an O₂ source (Peng *et al.*, 2005). Decreasing the O₂ content in a mixture of Ar (1 sccm flow of O₂ in 200 sccm flow of Ar) resulted in 1-D nanostructures as shown in Fig. 3(b) (Peng and Chen, 2004). However, the resultant nanostructures were not properly aligned and the coverage of the nanostructures was not high enough. Both chain-like and ribbon-like nanostructures were seen on samples oxidized in low concentration of oxygen in Ar atmosphere. The oxygen content was further decreased by using oxygen containing species such as water (H₂O), acetone (CH₃COCH₃), ethanol (CH₃CH₂OH), acetaldehyde (CH₃CHO), and dibutyltin dilaurate (C₃₂H₆₄O₄Sn) vapor in Ar to obtain higher coverage of 1-D nanostructures. The presence of water (H₂O) vapor in Ar resulted in micro-crystalline fibers as shown in Fig. 3(c) (Peng *et al.*, 2005). On the other hand, acetone (CH₃COCH₃) vapor in Ar resulted in dense and well-aligned array of 1-D TiO₂ as shown in Fig. 3(d) (Peng and Chen, 2004; Peng *et al.*, 2005). Similarly, presence of ethanol (CH₃CH₂OH), acetaldehyde (CH₃CHO), dibutyltin dilaurate (C₃₂H₆₄O₄Sn) vapor in Ar resulted in dense and aligned 1-D TiO₂ nanostructures (Peng *et al.*, 2005; Peng and Chen, 2005).

The effect of O₂ content during thermal oxidation of Ti alloys such as Ti64 substrates were studied for the growth of 1-D nanostructures (Arafat *et al.*, 2013). It was found that Ti64 alloys are capable of growing 1-D nanostructures at higher oxygen concentrations compared with α -Ti substrates. The coverage of 1-D nanostructures was optimum in presence of tens of ppm O₂ in Ar at a flow rate of 500 sccm (Arafat *et al.*, 2013, 2015). Increasing the O₂ content up to 500 ppm resulted in 1-D nanostructures on Ti64 substrate but the coverage is greatly reduced (Dinan *et al.*, 2013). Though the growth window of 1-D nanostructures is wider for Ti64 and β -Ti (5–5–5) substrates, pure oxygen resulted in oxide scales in all samples instead of 1-D nanostructures.

Effects of Temperature

The optimum growth temperature of 1-D nanostructures on Ti is in the range of 700–850 °C (Huo *et al.*, 2009; Peng and Chen, 2004; Peng *et al.*, 2005; Kaewsai *et al.*, 2010). The variation in the reported results in optimum oxidation temperature could be due

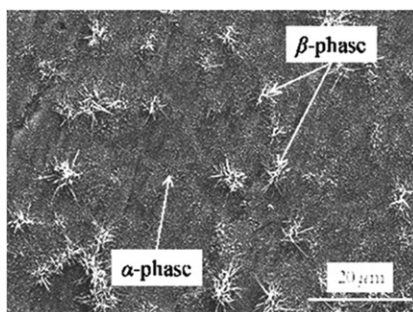


Fig. 2 The surface of Ti-6.85Al-1.6V substrate after thermal oxidation at 700 °C for 8 h at a flow rate of 500 sccm. The substrate contain α and β phase of Ti. 1-D nanostructures were preferentially grown on β phase during thermal oxidation (Lee *et al.*, 2010).

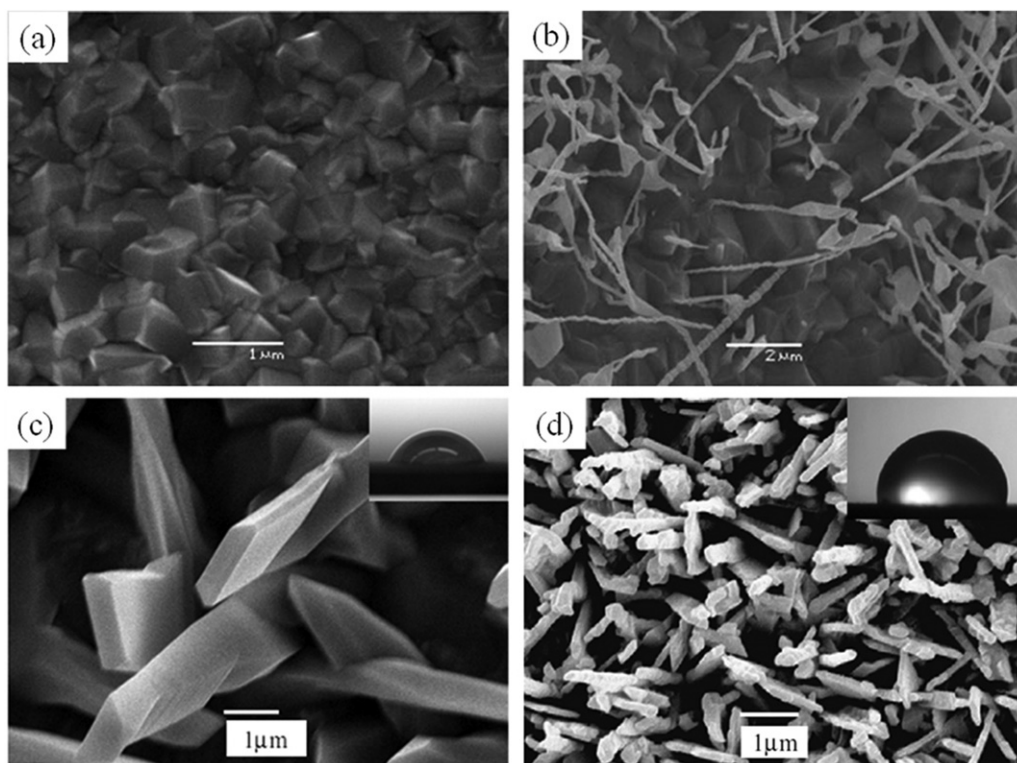


Fig. 3 TiO_2 nanostructures grown on Ti foil by thermal oxidation at 850°C in presence of different oxygen sources (a, b) pure oxygen (99%) and 1 sccm flow of O_2 in 200 sccm flow of Ar, respectively (Peng and Chen, 2004) and (c, d) water vapor and acetone in flowing Ar, respectively (Peng et al., 2005).

to the variations of impurities in commercial substrates or difference in experimental setup. However, all studies confirmed that thicker structures yielded at temperatures above the optimum (Daothong et al., 2007). As an example, Fig. 4 shows the variation in diameters of as-grown 1-D nanostructures on Ti wire oxidized in ethanol vapor at different temperatures (700 – 850°C) (Daothong et al., 2007). It was seen that the diameter of the 1-D nanostructures were 23 nm at the optimum growth temperature of 750°C . Increasing the oxidation temperatures to 850°C increased the diameter to of 73 nm. Further increment of temperature to 900°C in presence of dibutyltin dilaurate in Ar resulted in the formation of micro-whiskers (Peng and Chen, 2005).

Almost similar phenomenon was observed for Ti alloy substrates (Ti64 and β -Ti (5–5–5)) substrate during thermal oxidation. The optimum growth of 1-D nanostructures were found in the range 700 – 750°C (Arafat et al., 2013; Lee et al., 2010). Increasing the temperatures to 800°C or above resulted in a mixture of faceted and 1-D nanostructures. It was proposed that at low temperatures the oxidation is driven by anisotropy with preferential growth on certain crystal faces. This anisotropy decreases at higher temperature promoting growth on other surfaces leading to faceted crystals (Lee et al., 2010).

Effects of Oxidation Time

The effects of oxidation time for the growth of 1-D nanostructures on Ti and its alloy substrates were not studied extensively. However, it has been found that the length of the nanostructures increased with the increase of the oxidation time (Peng et al., 2005; Peng and Chen, 2004; Daothong et al., 2007). As an example, when acetone was used as the oxygen source at 850°C , short and oriented dots emerged during 12 min of oxidation of Ti substrates. Increasing the oxidation time to 30 min led to the formation of dense and short 1-D nanostructure arrays. Further increasing the time to 90 min resulted in long array of 1-D nanostructures. However, in the literature the maximum time for thermal oxidation was 8 h and a good amount of 1-D nanostructures were seen within this oxidation time (Lee et al., 2010; Dinan et al., 2013; Arafat et al., 2013, 2015). Extension of oxidation time beyond 8 h was not investigated for Ti and its alloy substrates. It should be noted that on Cu substrates the coverage of 1-D nanostructures decreased after reaching an optimum value at 5 h of oxidation time (Wu et al., 2014). Similar behavior is anticipated for the thermal oxidation of Ti and its alloy substrates.

Effects of Residual Stress

It was reported that the presence of residual stress on Cu substrates significantly improved the 1-D growth during thermal oxidation (Mema et al., 2011). However, no such systematic study was conducted for α -Ti substrates. But, oxidation of Ti64 substrates confirmed the significance of residual stress on 1-D growth (Arafat et al., 2013). It was shown that increase of residual

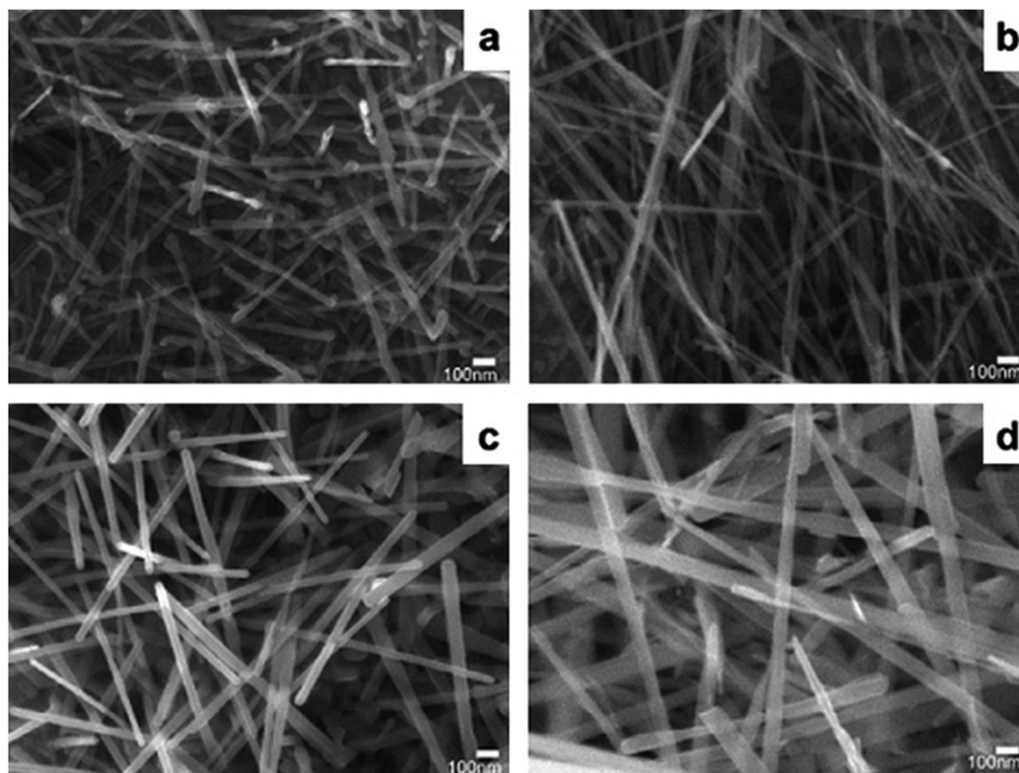


Fig. 4 SEM images of the as-grown 1-D nanostructures on Ti wire by thermal oxidation using ethanol vapor at different temperatures (a) 700 °C, (b) 750 °C, (c) 800 °C, and (d) 850 °C (Peng and Chen, 2005).

stress induced by milling or hammering improves the coverage of 1-D nanostructures on Ti64 substrate (Arafat *et al.*, 2013). Milling of Ti64 particles in planetary ball mill for 20 h followed by oxidation under optimum conditions significantly improves the 1-D growth compared with as-received particles as shown in Fig. 5 (Arafat *et al.*, 2013). The length of the 1-D nanostructures after thermal oxidation grown on as-received Ti64 particles possessed length of 500 nm (Fig. 5(a)) which increased to 1–5 μm (Fig. 5(b)) in the milled particles followed by thermal oxidation (Arafat *et al.*, 2015). Stress measurement by XRD- $\sin^2\psi$ technique revealed that the compressive stress was significantly increased inside the milled particles prior to thermal oxidation (Arafat *et al.*, 2013). The compressive residual stress in milled particles was released during thermal oxidation by creating new surfaces such as 1-D nanostructures (Arafat *et al.*, 2013).

To further elucidate the effect of residual stress on 1-D growth, a Ti64 plate was hammered at one end (right corner as shown in Fig. 6(a)) and the other end was un-hammered. A gradient of stress was created by hammering from one end to another of Ti64 plate. Thermal oxidation was carried out on the plate at 750°C for 8 h with 40 ppm oxygen at a flow rate of 500 sccm. Investigations under FESEM revealed that the growth of 1-D nanostructures gradually increased from un-hammered end to the hammered end as shown in Fig. 6(b–e). This experiment clearly supports the stress induced growth of 1-D nanostructures on Ti64 substrate.

Characterization of the 1-D Nanostructures

During thermal oxidation of Ti and its alloys, an oxide scale formed on the substrates and 1-D nanostructures evolved on top of the oxide scale. Characterizations of the oxide scale on the substrate and 1-D nanostructures are discussed separately in the following sections.

Characterization of the Oxide Scale beneath 1-D Nanostructures on Ti and Its Alloys

It is well known that thermal oxidation of pure Ti in air or pure oxygen resulted in TiO_2 layer without having any 1-D nanostructures. Very low concentration of oxygen or oxygen containing medium is required for the growth of 1-D nanostructures on α -Ti substrates. So far, no study revealed the state of the oxide scale on the α -Ti substrate in oxygen deprived conditions for the growth of 1-D nanostructures, but it was presumed to be an oxide scale of TiO_2 . Other states of oxides were not reported in the literature during thermal oxidation of α -Ti for the growth of 1-D nanostructures (Chen and Mao, 2007; Peng *et al.*, 2005).

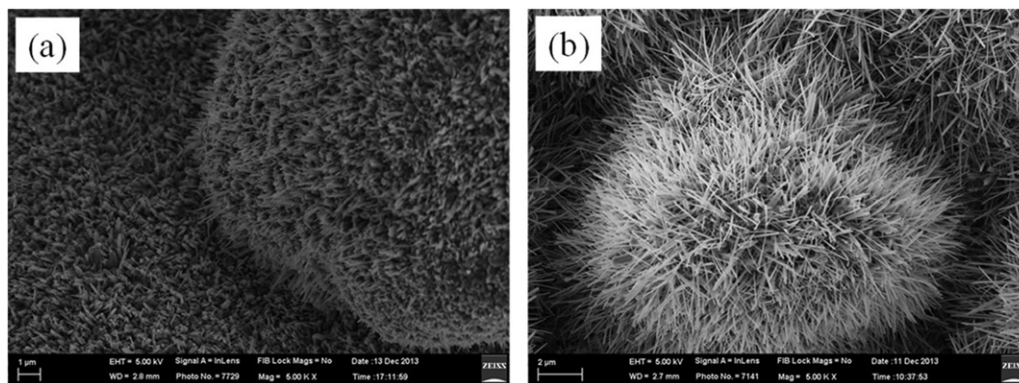


Fig. 5 FESEM images of the thermally oxidized Ti64 particles under optimum conditions (a) as-received and (b) particles milled for 20 h.

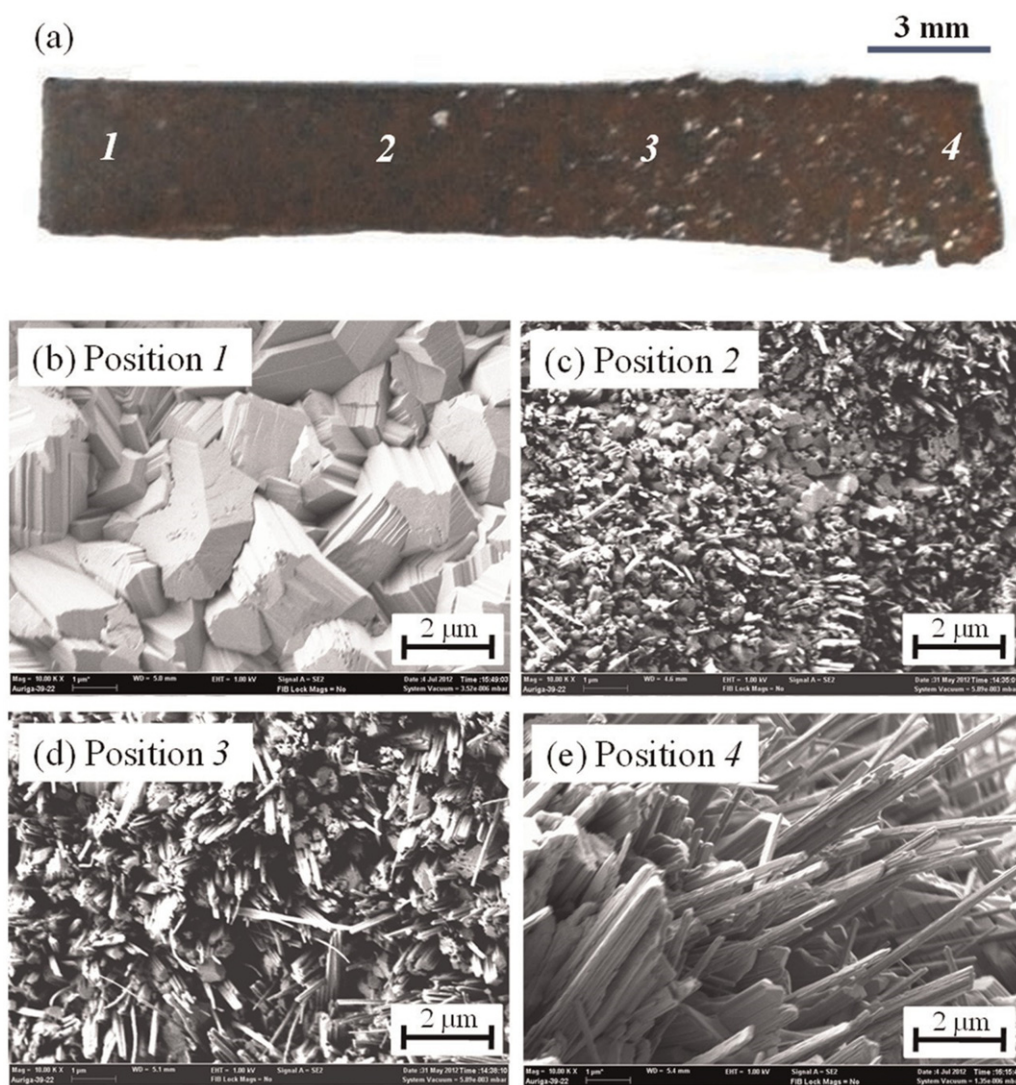


Fig. 6 (a) Ti64 sheet (25 μm $\times$ 3 μm $\times$ 1 μm) hammered at one end (right corner), and FESEM micrograph on the Ti64 sheet after thermal oxidation at (b) position 1, (c) position 2, (d) position 3, and (e) position 4 (Arafat et al., 2013).

In the case of Ti64 substrate, a double layer of oxides was formed on the substrate in oxygen deprived conditions for the growth of 1-D nanostructures as shown in Fig. 7(a) (Arafat *et al.*, 2015). The outer oxide layer is a mixture of TiO_2 and Al_2O_3 and the inner oxide layer is only TiO_2 , which was confirmed by EDS analysis as shown in Fig. 7(b–e). It was also shown that the thickness of the outside oxide layer increases with the increase of the size of Ti64 particles. It is worth noting that the double layer of oxides was also evident during oxidation of Ti64 in air though no 1-D nanostructure was observed at the outer layer (Guleryuz and Cimenoglu, 2009). It was claimed that during thermal oxidation of Ti64 substrate, Al diffuses outward and oxygen diffuses inward which could be a reason of Al depletion from the inner oxide scale (Guleryuz and Cimenoglu, 2009). The TiO_2 - Al_2O_3 phase diagram shows that the TiO_2 and Al_2O_3 are completely immiscible and no solid solutions or intermetallic compounds are formed at the temperatures of 1-D growth (700–850 °C) (Cano *et al.*, 2007). So, it is believed that Al_2O_3 and TiO_2 grains are present in the outer oxide scale though the exact distribution of the oxides is not clear and further research is required.

Characterization of 1-D Nanostructures

During thermal oxidation of Ti and its alloys, oxide scales were formed on the substrate. Under optimum conditions, 1-D nanostructures formed on the top surface of the oxide scales. The as-grown nanostructures were straight with no entanglement. The diameter and length of the 1-D nanostructures were in between 15–200 nm and 1–5 μm , respectively (Table 1). The difference in results was attributed to different experimental conditions such as variations in temperatures and oxidation time. Depending on the alloy conditions and oxidation medium, different types of 1-D nanostructures were grown on the top surface of the oxide scale. When oxygen was used at very low concentrations or water vapor was used, the resulting 1-D nanostructures were TiO_2 only (Peng and Chen, 2004; Peng *et al.*, 2005). However, presence of acetone vapor as oxidation medium resulted in quasi-aligned 1-D nanostructure consisting of TiO_2 core and carbon (C) shell as shown in Fig. 8(a–b) (Huo *et al.*, 2008, 2009). It was proposed that acetone decomposes to CH_3 and CO at the oxidation temperatures (Montoro *et al.*, 2007). The CO preferentially adsorbed on the surface of Ti substrate and reacts to form TiO_2 and amorphous C (Daothong *et al.*, 2007). The amorphous C at the shell can be removed by annealing the 1-D nanostructures in air at 650 °C for 30 min (Huo *et al.*, 2009). Similarly, when ethanol was used as the oxidation medium presence of C was found in Raman spectra (Daothong *et al.*, 2007). However, no carbon coating was observed on the 1-D TiO_2 nanostructures. So, it was claimed that the carbon peaks in Raman spectra were attributed for the deposition of carbon on the oxide scale (Daothong *et al.*, 2007).

Oxidation of Ti64 substrate under optimum conditions for the growth of 1-D nanostructures yielded TiO_2 core and Al_2O_3 shell as shown in Fig. 8(c) (Arafat *et al.*, 2015; Dinan *et al.*, 2013). It should be noted that Ti64 samples contained 6 wt% of Al with 4 wt % of V. During the oxidation process, both Al and Ti were oxidized forming TiO_2 as core and Al_2O_3 as the shell of 1-D nanostructure. The HRTEM image of Fig. 8(c) is shown in Fig. 8(d) and it reveals the (1 2 2) crystal planes confirming the presence of corundum Al_2O_3 at the shell of the 1-D nanostructures (Arafat *et al.*, 2015).

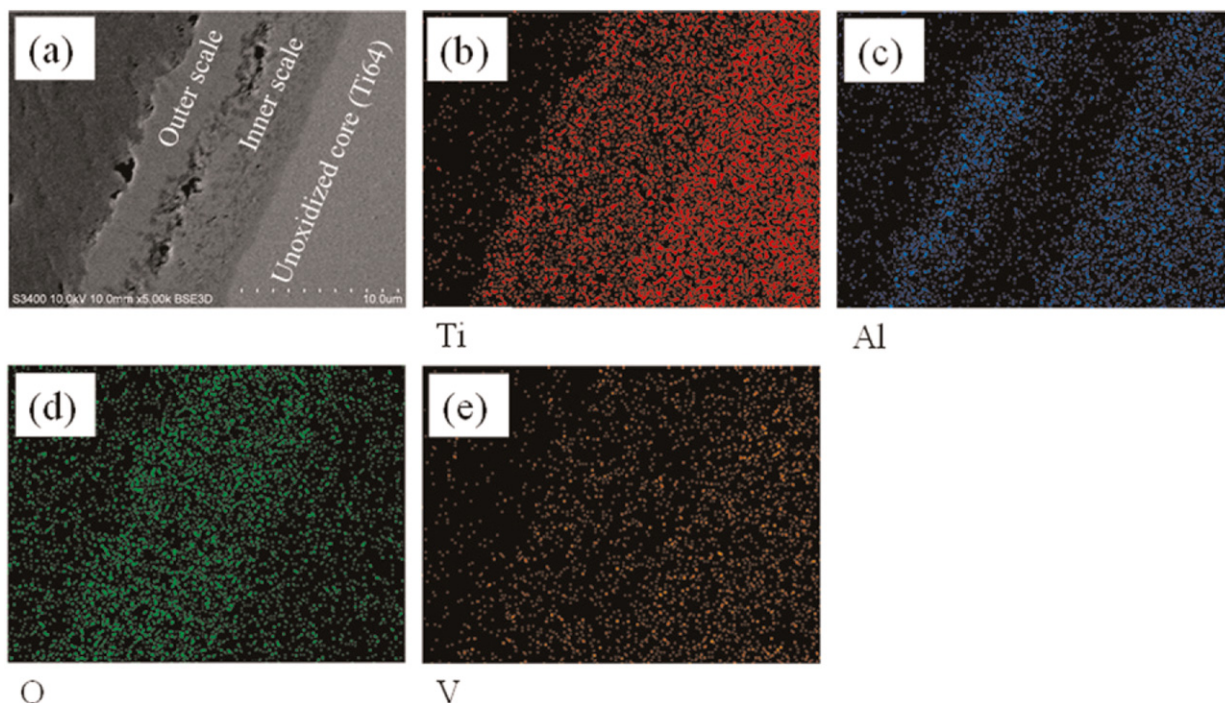


Fig. 7 (a) SEM image of the cross-section of Ti64 particles after thermal oxidation at 750 °C for 8 h with 15 ppm of O_2 in flowing Ar (500 sccm) and corresponding EDS elemental mapping of (b) Ti, (c) Al, (d) O, and (e) V (Arafat *et al.*, 2015).

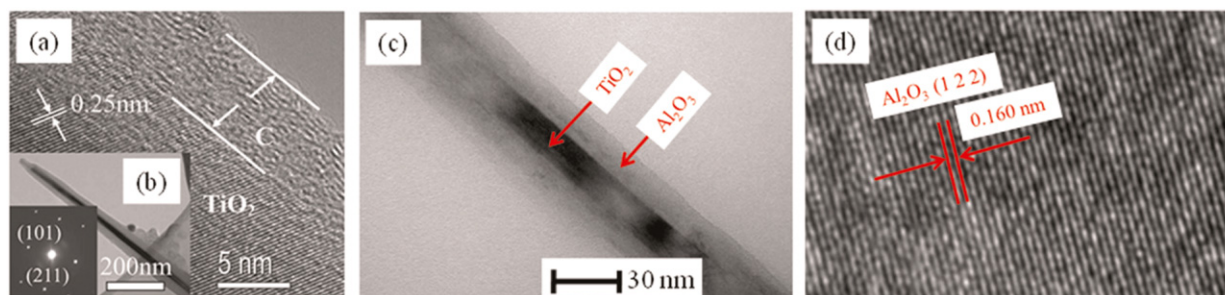


Fig. 8 (a) High resolution TEM image of the 1-D core/shell TiO_2/C nanostructure grown on Ti substrate using acetone as oxidation medium, and (b) corresponding low magnification view and SADE pattern (Huo et al., 2008), (c) TEM image of the 1-D core/shell $\text{TiO}_2/\text{Al}_2\text{O}_3$ nanostructure grown on Ti64 substrate using 15 ppm O_2 in flowing Ar, and (d) corresponding HRTEM image showing lattice fringes of Al_2O_3 shell (Arafat et al., 2015).

Regardless of the substrates, in all cases rutile structure of TiO_2 was obtained in the 1-D nanostructures during thermal oxidation. In most of the cases, the $[0\ 0\ 1]$ growth direction of TiO_2 was reported in the literature (Table 1). However, exceptions were found in growth direction of TiO_2 and reported as $[1\ 0\ 1]$ by Huo et al. (2008). Though different terminology was used in the literature to denote the 1-D nanostructures, in all cases the morphology of the structures were almost the same for a given experimental condition.

Growth Mechanism of 1-D Nanostructures

The oxidation temperature and atmosphere has remarkable effect on the growth of 1-D nanostructures on Ti substrates (Peng and Chen, 2004). According to Peng et al. (2005), the oxidation of Ti substrate may occur at the gas-oxide interface, inside the oxide scale and/or oxide-metal interface (Peng et al., 2005). The conditions for the growth of 1-D nanostructures on Ti substrate might be influenced by four factors (Peng et al., 2005):

1. active oxygen species diffuse from the gas-oxide interface to oxide-metal interface through grain boundaries;
2. diffusion rate of Ti atoms from the oxide-metal interface to gas-oxide interface through the grain boundaries;
3. diffusion rate of active oxygen species and Ti atoms on a specific crystal plane; and
4. the amount of available active oxygen species.

According to this growth model, Ti substrate is oxidized at the beginning to form a thin film of TiO_2 grains and the diffusion process of oxygen and titanium through the grain boundaries of TiO_2 is governed by the morphology of formed TiO_2 (Chen and Mao, 2007; Peng et al., 2005). There is predominant diffusion of oxygen through the grain boundaries of the oxide layer at temperatures 800–1000°C and the reaction occurs at the metal-oxide interface (Badescu and Mormirlan, 1996). At temperatures above 1000°C, a considerable increase in the diffusion of Ti cations through the oxide layer is observed.

On the other hand, Czerwinski and Szpunar (Czerwinski and Szpunar, 1998) showed that TiO_2 growth at 900°C is controlled by the surface diffusion of Ti cations to the ledges located on the sidewalls of pyramidal grains. So, it is reasonable to assume that at the oxidation temperatures (700–850°C) for the growth of 1-D nanostructures on Ti substrates, oxygen diffuses to the oxide-metal interface in the presence of high oxygen concentration such as pure oxygen or formic acid. For this reason, only polycrystalline films of oxide is formed instead of 1-D nanostructures. In contrast, when ethanol, acetaldehyde, or acetone is used as the oxygen source, the active oxygen species is expected to be less abundant. This allows Ti atoms sufficient time to diffuse to the gas-oxide interface through grain boundaries. The diffused Ti atoms then react with the selectively adsorbed oxygen species on different planes of rutile TiO_2 (Diebold, 2003), resulting in the formation of 1-D nanostructures along certain direction on the substrate. Due to the high surface energy, the freshly formed TiO_2 particles are good seed sites for subsequent growth in 1-D by the continuous supply of O_2 species.

Presence of residual stress enhances the coverage of 1-D nanostructures in thermal oxidation process. The effect of residual stress of Ti64 particles were measured by XRD- $\sin^2\psi$ technique and it was shown that the coverage of 1-D nanostructures were significantly enhanced in the stressed particles (Arafat et al., 2013). It was proposed that energy required to form fresh surface was provided by the interaction of metal with the surrounding atmosphere. A stressed surface releases its residual stress by creating new surfaces such as 1-D nanostructures.

Summary and Conclusions

1-D nanostructures of TiO_2 is being used in different engineering applications such as gas sensors, solar cells, super capacitors, lithium ion batteries due to their superior physical, chemical, and electronic properties. Single phase and nanocomposite TiO_2 can be synthesized by an inexpensive and highly scalable procedure named thermal oxidation. The process is very simple and requires only

Table 2 Comparison of oxidation parameters and resultant morphologies of 1-D nanostructures grown on Ti and Ti64 substrates during thermal oxidation

Processing, physical, and chemical characteristics	Ti	Ti-6Al-4V (Ti64)
Oxygen as oxidizing environment	Very low (<10 ppm) concentration of oxygen was required at a flow rate of 200 sccm or less. High concentration of O ₂ produced oxide scale instead of 1-D nanostructures	1-D nanostructures were observed up to 500 ppm of oxygen at a flow rate of 1000 sccm or more. The coverage of 1-D nanostructures decreased with increasing the concentration of oxygen and flow rate
Water, formic acid, acetone, ethanol, acetaldehyde, and dibutyltin dilaurate as oxidizing agent	No 1-D structure was observed for formic acid. Acetone, ethanol, acetaldehyde, and dibutyltin dilaurate yielded higher coverage of 1-D nanostructures	Not studied
Optimum growth temperature	700–850 °C	700–750 °C
Oxidation time	Maximum oxidation time reported in the literature was 8 h.	Studies were not conducted beyond this time frame
Effects of residual stress	Not studied	Compressive residual stress significantly improved the coverage of 1-D nanostructures
Coverage of 1-D nanostructures	Low to medium	High
Morphology of the 1-D nanostructures	Single 1-D TiO ₂ was observed when oxygen at very low concentrations or water vapor in Ar was used as oxidation medium. However, acetone as an oxidation agent yielded 1-D core-shell TiO ₂ -C	D core-shell TiO ₂ -Al ₂ O ₃ was obtained when low concentration of oxygen in Ar was used as oxidation medium. Studies were not conducted by using oxygen containing hydrocarbons as oxidizing medium
Crystal structure of the 1-D nanostructures	Single TiO ₂ : rutile. Core-shell TiO ₂ -C: rutile-amorphous	Core-shell TiO ₂ -Al ₂ O ₃ : rutile-corundum
Growth direction of the 1-D nanostructures	[0 0 1] and [1 0 1] were reported	[0 0 1] was reported in one study
Oxide scales beneath the 1-D nanostructures	Only TiO ₂ was formed	A double layer of oxides were formed beneath the 1-D nanostructures. The outer oxide scale was composed of TiO ₂ and Al ₂ O ₃ whereas the inner oxide scale is solely TiO ₂
Growth mechanism		No conclusive study was performed

heating the substrate in an atmosphere containing very low concentration of O₂, water vapor, acetone, ethanol, acetaldehyde, or dibutyltin dilaurate in Ar. Pure Ti and a number of Ti alloy substrates such as Ti-6Al-4V, 5Al-5V-5Mo-3.5Cr-0.5Fe, Ti-6.85Al- 1.6V were studied for thermal oxidation process, but most of the studies focused on pure Ti and Ti-6Al-4V alloys. Ti-6Al-4V and 5Al-5V-5Mo-3.5Cr-0.5Fe alloys containing β phase showed higher coverage of 1-D nanostructures compared with pure Ti with α phase. A comparison of 1-D nanostructures on pure Ti and Ti-6Al-4V alloy in terms of process parameters and morphology is summarized in [Table 2](#).

During oxidation, oxide scales were formed on the substrates. The 1-D nanostructures grew in outward directions on the top surface of an oxide scale. The parameter window for 1-D growth was wider for the Ti64 alloy compared with the pure Ti. Very low concentration of oxygen was required for the 1-D growth on pure Ti substrate as shown in [Table 2](#). However, the 1-D nanostructures were not properly aligned and the coverage was not sufficient. Lowering the oxygen concentration by using water, acetone, ethanol, acetaldehyde, or dibutyltin dilaurate yielded increased amount of 1-D nanostructures on pure Ti substrates. The resultant nanostructures were single phase 1-D TiO₂ when oxygen in Ar or water vapor in Ar was used as the oxidizing medium. 1-D core-shell TiO₂-C formed when acetone was used as an oxidizing agent. Only a single phase oxide scale of TiO₂ was formed beneath the 1-D nanostructures on pure Ti substrate.

When Ti-6Al-4V alloy was oxidized in low concentration of oxygen, the nanostructure was 1-D core-shell TiO₂-Al₂O₃. The resultant nanostructures were straight with no entanglement. A double layer of oxides were formed beneath the 1-D nanostructures on Ti-6Al-4V substrates. The outer layer was composed of a mixture of TiO₂ and Al₂O₃ whereas the inner oxide scale was solely TiO₂. Residual compressive stress significantly improved the 1-D growth and coverage on Ti-6Al-4V substrates.

Regardless of the substrate and oxidation medium, in all cases rutile phase of TiO₂ was obtained by the thermal oxidation process. It was proposed that during thermal oxidation Ti atom diffuses to the gas-oxide interface through grain boundaries and reacts with the oxygen on specific crystal plane of rutile forming 1-D nanostructures. However, this mechanism is not fully established and further studies are required.

Acknowledgment

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Laser Induced Graphene: New Sensing Applications

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Abstract

The application of Laser Induced Graphene (LIG) to a multitude of sensing applications is outlined. A discussion of the material origins and the intrinsic properties that make it optimal for sensing is followed by analyses of exemplar motion, chemical and biological sensors from the literature. The rapid growth of research output on LIG sensors is warranted due to the remarkable capabilities of such a cost effective and easily manufactured substrate. Subject to standardization of manufacturing, LIG may achieve commercial viability where prior graphene based materials have fallen short.

Nomenclature

Abbreviation	Definition
AC	Alternating Current
Ag/AgCl	Silver/Silver Chloride
AMR	Antimicrobial Resistance
CFU	Colony Forming Units
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
diH ₂ O	Deionized Water
DNA	Deoxyribonucleic Acid
DPV	Differential Pulse Voltammetry
DVD	Digital Versatile Disk
E. Coli	Escherichia coli
ECG	Electrocardiogram
EEG	Electroencephalogram
EMG	Electromyogram
EPPG	Edge Plane Pyrolytic Graphite
GBM	Graphene Based Materials
GO	Graphene Oxide
GOx	Glucose Oxidase
HET	Heterogenous Electron Transfer
IR	Infrared
LIG	Laser Induced Graphene
MIP	Molecularly Imprinted Polymer
miRNA	Micro Ribonucleic Acid
ORR	Oxygen Reduction Reaction
P. Aeurginosa	Pseudomonas aeruginosa
PAA	Polyamic Acid
PBS	Phosphate Buffered Saline
PDMS	Polydimethylsiloxane
PEDOT	poly(,4-ethylenedioxythiophene)
PI	Polyimide
RT-PCR	Real Time Polymerase Chain Reaction
S. Aureus	Staphylococcus aureus
SARS-CoV-2	Severe Acute Respiratory Syndrome Coronavirus 2
SEM	Scanning Electron Microscopy
SPCE	Screen Printed Carbon Electrodes
SPE	Screen Printed Electrode
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy

Key Points

- To provide a concise overview of laser induced graphene.
- To highlight the adoption of the material in cutting edge sensing applications.
- To place the material in context of competing technologies.
- To critically appraise the performance of the material and highlight future directions.

Introduction

Since its discovery and initial characterization in 2004 (Novoselov, 2004), graphene has been heralded as a wonder substance that promises to exert influence, if not revolutionize, almost every technological sector. There is an enormous literature base dedicated to its preparation, characterization, modification and application, and a discussion on any one these topics, or even a subset, could easily fill many volumes. The functional versatility (mechanical, electrical, thermal, optical) of the material and its adaptability across multiple sectors has similarly stimulated considerable commercialization opportunities. This stands in marked contrast to the other carbon allotropes – fullerene and carbon nanotubes, both of which proffered new technological vistas at the time of discovery but, arguably, have yet to make substantive commercial breakthroughs. Graphene based materials have bridged to a diverse portfolio of consumer products and some of these are listed in Table 1.

The degree of interest in graphene, at least from a research perspective can be crudely evaluated through comparing the emergence of research publications over the past decade or so. The rate of growth is highlighted in Fig. 1 and is compared alongside other recent advances in carbon nanomaterials. The ubiquity of graphene and, indeed, the demand for the material for investigative purposes has been facilitated through an abundance of recipes for its production but, there can be many pitfalls – especially in terms of time, instrumentation overheads, expertise, end product quality and issues of reproducibility. A multitude of graphene “manufacturers” have emerged in recent years with many hundreds of graphene-based materials (GBM) available off the shelf or produced to demand but, there is no common agreement on the most important parameters needed to compare these different materials. Although a tentative classification framework has been proposed for 2D GBM, standardization remains elusive (Kovtun *et al.*, 2019).

The emergence of laser induced graphene (LIG), in contrast to many of the bench techniques for the production of GBM, has offered a new fabrication strategy which, at least in terms of electronic applications, could serve as a relatively accessible foundation for the speedy development of smart biomedical devices. The acquisition of a standard for LIG, just as with the other 2D GBMs is still contentious and dependent on a host of factors and, as such, this review aims to train a spotlight on the various

Table 1 Examples of commercial products incorporating graphene or graphene based materials

Product Type	Manufacturer/Supplier	Function
Smartphone	Huawei	Processor cooling
Earphones	Versarien	Speaker diaphragm
Phone Case	NanoCase	Thermal dissipation
Portable Device Charger	Real Graphene	Thermal dissipation and electrical conduction
Smart watch	Wuxi	Conductive touchscreen
Solid State Drive	Team Group	Thermal dissipation
Watch	Richard Mille	Integrated Structural support and anti-static
Lightbulb	Sera	Thermal dissipation
3D Printing Filaments	Add North 3d	Integrated structural support
Field Effect Biosensor	Nanomed	Sensing surface
Heat Therapy Belt	Xiaomi	Thermal dissipation
Antibacterial Facemasks	IDEATI	Antistatic and antibacterial
Pillow	Cecorelax	Thermal dissipation
Car	Briggs Motor Company	Integrated structural support
Tyres	Vittoria	Integrated structural support and heat dissipation
Bus / Train / Crane / Elevator	Skeleton Technologies	Ultracapacitors (Kinetic Energy Recovery System)
Supercapacitors	Urbix Resources	Conductivity and capacitance
Tennis Racket	HEAD	Integrated structural support
Bike	Dassi Bikes	Integrated structural support
Chain Lubricant	ABufferuteBlack	Oxidation resistance and water repulsion
Hockey Stick	Grays	Integrated structural support
Wetsuit	Billabong	Thermal conductivity
Bulletproof vest	IDEATI	Integrated structural support
Sportswear	Colmar	Thermal conductivity and antibacterial
Glasses	Ray-Ban	Integrated structural support

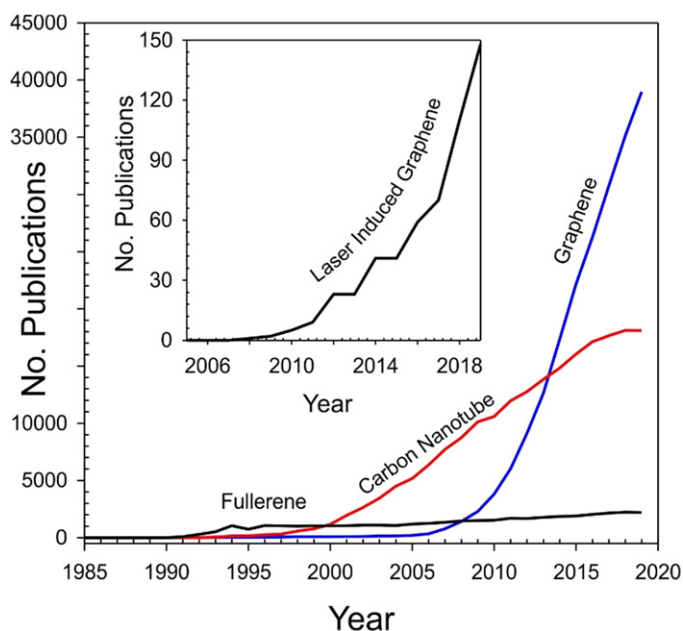


Fig. 1 Publications recorded in Thomson ISI Web of Science Database containing fullerene, carbon nanotube or graphene. Inset: Publications relating to the laser induced graphene.

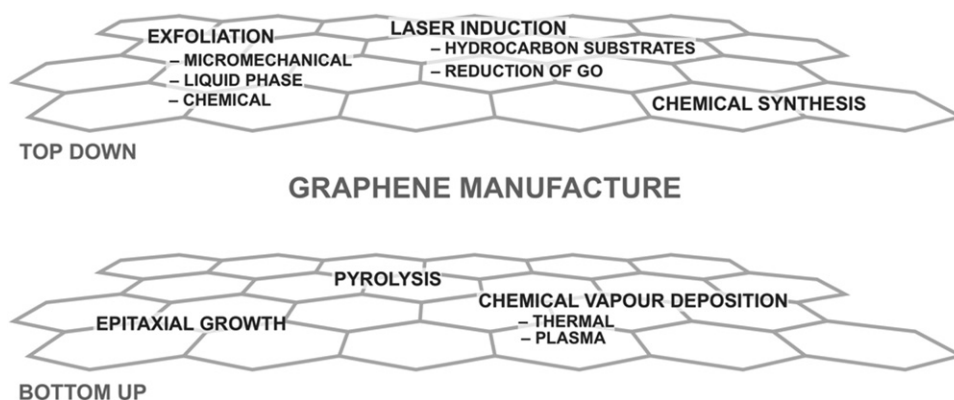


Fig. 2 Graphene based material production methods.

procedures associated with LIG production. Moreover, a critical assessment of the various merits and limitations of the approach in terms of device design, rapid prototyping and potential applications of the technology are considered.

Evolution of Laser Induced Graphene

Chemical vapor deposition (CVD) is often associated with the production of graphene and a large variety of metallic substrates have been employed to facilitate its production but, while effective, the process lacks the accessibility required for widespread adoption. It is little surprise that a large number of alternative approaches have arisen and some of these are summarized in Fig. 2. A critical assessment of the relative merits of each is beyond the scope of the present discussion and the reader is directed to more comprehensive reviews for insights into the respective practical and performance characteristics of the different techniques. It must be noted that, despite a considerable variety of production strategies, few provide spatial control over the deposition of the graphene component. The inability to pattern graphene structures with a high degree of precision has been particularly problematic, when considering the small (micro-nano) dimensions common to the new generation of smart devices.

The emergence of low-cost laser scribing technology, however, effectively counters such issues enabling close control over both the patterning and physico-chemical properties of the graphene structures. This can enable the direct integration of graphene within devices from the macro to micro scale using desktop diode laser systems that can cost less than £100. Clearly, the expense

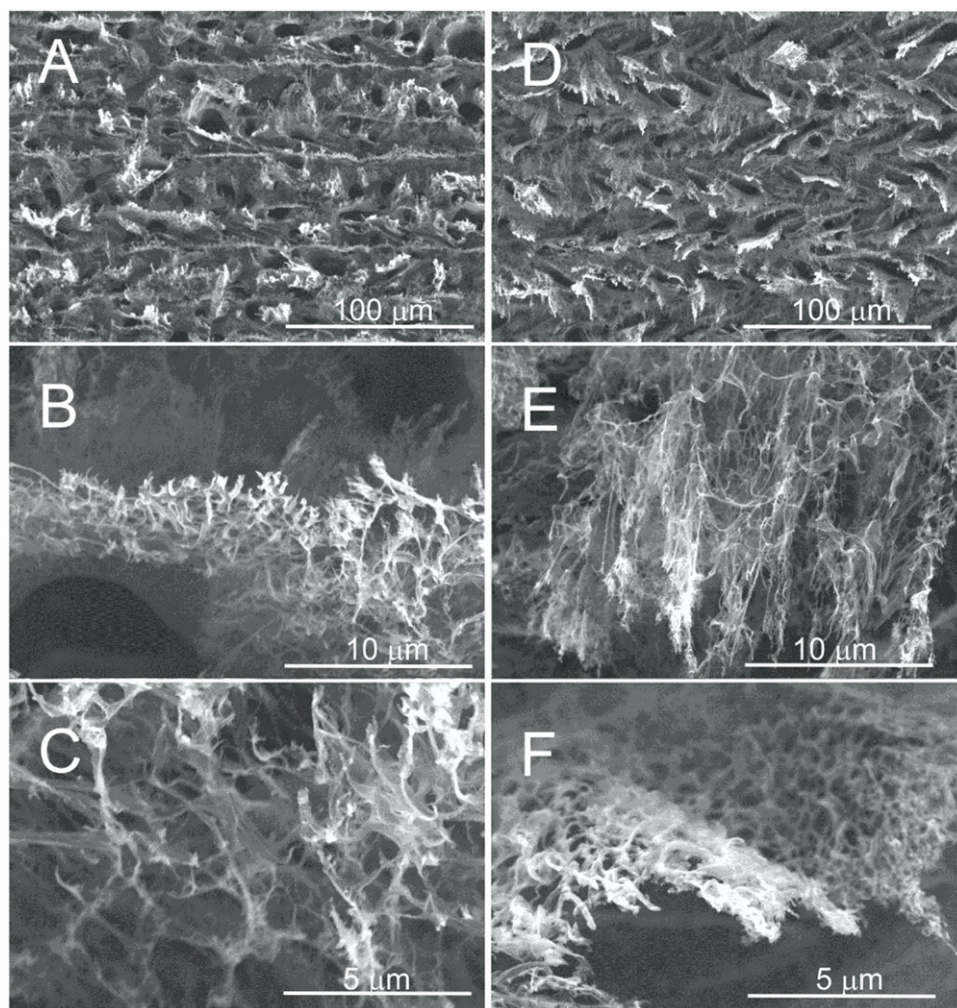


Fig. 3 SEM images of LIG film on polyimide are being subjected to 1 laser raster (A-C) and after 5 repetitive sweeps (D-F). Reproduced from Barber, R., Cameron, S., Devine, A., *et al.*, 2021. Laser induced graphene sensors for assessing pH: Application to wound management. *Electrochemistry Communications* 123, 106914. Available at: <https://doi.org/10.1016/j.elecom.2020.106914>.

incurred in the instrumentation configuration (i.e. higher specification lasers) increases with the pursuit of precision but the accessibility of LIG has begun to make considerable inroads in device design (Inset, **Fig. 1**).

A scalable method for producing graphene in a pre-designed pattern with consistent morphology has long been sought for bioelectronic applications and the first steps towards the realization of this goal can be attributed to El-Kady *et al.* (2012), with the use of a commercial DVD optical drive. Their system exploited a laser to reduce a film of graphene oxide, to form graphene but this was still far from the easily accessible fabrication required. The need for the pre-processing of a graphene oxide film was removed, when the Tour research group pioneered a single-step process that generated a film of porous graphene onto an insulating polymer substrate (Lin *et al.*, 2014). The group were able to use a CO₂ infrared (IR) laser to fabricate electrodes for in-plane capacitors on a commercial polyimide (PI) film. The photothermal conversion of PI results in the rapid liberation of gaseous products which, at least initially, results in 3D foam like morphological features as highlighted in **Fig. 3**. The resulting material was found to exhibit a 2D Raman band (at 2700 cm⁻¹), characteristic of graphene and thus the term Laser Induced Graphene (LIG) was coined. The material consists of a few layers stacked along the c axis which gives rise to a 3D structure, this is in contrast to thermal CVD graphene where the graphene layers grow parallel to the catalyst surface (Chen *et al.*, 2011; Lin *et al.*, 2014). The LIG structures were found to possess a substantial surface area ($\approx 340 \text{ m}^2 \text{ g}^{-1}$) and excellent conductivity ($5\text{--}25 \text{ S cm}^{-1}$) (Lin *et al.*, 2014; Peng *et al.*, 2015) and thus set the foundations for a raft of new sensor applications.

Polyimide is intrinsically insulating but the abundance of aromatic groups within the polymer backbone (**Fig. 4**) and its wide absorption range has since enabled the use of UV, visible and IR laser scribing systems to carbonize the substrate surface and yield conductive tracks (Inagaki *et al.*, 2013; In *et al.*, 2015). The “off the shelf” accessibility of PI films covering a wide spectrum of relatively low cost forms (particularly films and tapes of various thickness) also provides tremendous flexibility in design and facilitates rapid prototyping. This can be exemplified by the transition from the computer aided design of the proposed pattern to

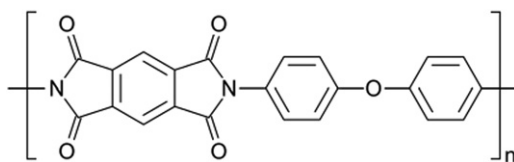


Fig. 4 Chemical structure of Polyimide (Kapton®). Reproduced from Inagaki, M., Ohta, N., Hishiyama, Y., 2013. Aromatic polyimides as carbon precursors. *Carbon* 61, 1–21. Available at: <https://doi.org/10.1016/j.carbon.2013.05.035>.

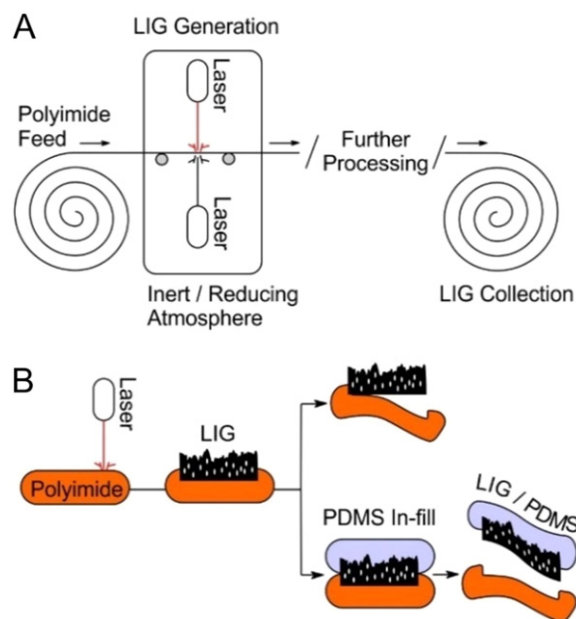


Fig. 5 (A) Roll to roll production of LIG structures and (B) Production of freestanding or composite LIG films.

its actual formation on the substrate being in the order of minutes. This speed of fabrication, absence of chemical pre-treatments and the exploitation of commercial substrates and laser systems are clear advantages and the combination of these factors stands in marked contrast to the time intensive nature of many of the techniques highlighted in Fig. 2.

It should also be noted that the formation of LIG is not restricted solely to PI substrates and alternatives such as polyetherimide (PEI) (Lin *et al.*, 2014), poly (ether ketone) (PEEK) (Zhu *et al.*, 2019), polysulfone (PSU) (Zhu *et al.*, 2019), cross-linked polystyrene (PS) (Chyan *et al.*, 2018), tar (Zang *et al.*, 2020) and Teflon (Ye *et al.*, 2018a) have also been utilized. In addition, the use of substrates based on cellulose, coconut shell, potato (Chyan *et al.*, 2018), wood (Ye *et al.*, 2017), lignin (Lei *et al.*, 2020) testify to the versatility of the laser processing method however, it must be noted that reproducibility from feedstock materials that are inherently variable can be questionable. Manipulation of instrumental factors (i.e. power, scan speed, scan repetition) associated with the laser have been shown to influence the degree of carbonization and can significantly alter the morphology from macro porous foams to nanotube forests (Fig. 3). The atmospheric composition of the laser environment can also greatly impact on the surface wettability of the resulting film, through the introduction of chemical groups, where the contact angle can range from superhydrophilic (0° in O_2/Air) to superhydrophobic ($>150^\circ$ in Ar, H_2 , SF_6) (Li *et al.*, 2017).

The inclusion of heteroatoms (i.e., Boron-doping) is well established as a means of enhancing the capacitance performance of GBMs and the adoption of such strategies to LIG based systems has been successfully demonstrated by Tour *et al.* (Ye *et al.*, 2019). Rather than using commercial PI film, the custom formation from a polyamic acid (PAA) / boric acid mixture resulted in the formation of a PI film in which the borate components were homogeneously dispersed. Laser treatment of the latter yielded B-LIG with capacitance some 3-fold greater than the undoped control. The approach is not limited to boron and offers a generic route to the incorporation of catalytic particles through the simple mixing of the latter with the PAA solution to yield a range of custom PI films. The efficacy of the approach was demonstrated through the inclusion of Co_3O_4 , MoO_3 and Fe_3O_4 nanocrystals into LIG structures and the ability of the latter to catalyse the electrochemical oxygen reduction reaction (ORR) (Ye *et al.*, 2015). The latter facilitates the generation of reactive oxygen species such as peroxide or hydroxyl radical. The incorporation of precious nanocatalysts such as Pt or Au have also been used for the electrocatalytic reduction of peroxide in electroanalytical sensors (discussed later). Hence, judicious choice of the secondary components applied to the LIG matrix can allow the substrate to be uniquely tailored to particular applications.

The direct writing of the pattern to an appropriate substrate can at first thought appear to be a slow batch process but the adaptation of the approach to continuous roll to roll manufacturing (Fig. 5(A)) provides a pathway for the scalable production of

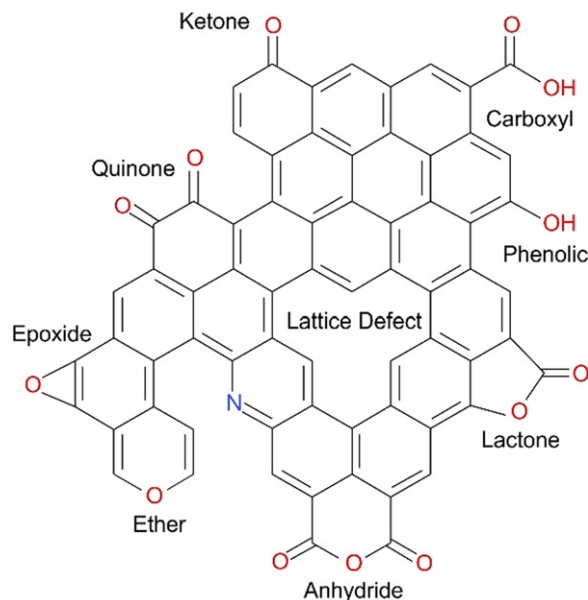


Fig. 6 Different functional groups and defects common to carbon based substrates. Reproduced from Casimero, C., Hegarty, C., McGlynn, R.J., Davis, J., 2020. Ultrasonic exfoliation of carbon fiber: Electroanalytical perspectives. *Journal of Applied Electrochemistry* 50 (3), 383–394. Available at: <https://doi.org/10.1007/s10800-019-01379-y>.

devices. The substrate roll (typically polyimide) can be irradiated on one or both sides by moving through a fixed CO₂ laser beam. The raw LIG formation can then be further processed (i.e. electrochemical / spray treatment) to include additional catalysts before being dried and collected in the take up roll. Post laser treatments have included the addition of MnO₂, FeOOH and polyaniline to enhance the performance of LIG based flexible supercapacitors (Li *et al.*, 2016) but, it is possible to envisage enzymes, antibodies, aptamers or single strand DNA being deposited on a continuous process in the fabrication of disposable sensing assemblies.

While the inherent mechanical flexibility of LIG based films created directly on PI substrates is widely proffered as an advantage, especially in the context of wearable sensors, a degree of caution is required. Adhesion of the former to the underlying substrate upon which it was created can be poor with repeated flexing leading to fracture and flaking. The application of a top coat of polymer (PDMS, EcoFlex™ etc) and the subsequent removal of the initial PI layer serves to create a much stronger composite laminate as highlighted in Fig. 5(B). The latter can significantly improve the mechanical properties of LIG and such materials have found roles in a diverse range applications including anti fouling/antibacterial membranes, joule heaters, resistive memory devices and a spectrum of sensor systems (Luong *et al.*, 2019).

In contrast to the flawless single layer honeycomb lattice structure normally used to represent graphene, the LIG structure contains a multitude of structural defects (Fig. 6) and, depending on the atmosphere used in its production, various chemical functionalities and heteroatoms can be introduced (Ye *et al.*, 2019). Such chemical features are common to carbon-based substrates but the relative population of each will depend on the fabrication process and the materials subsequent history. Graphene oxide (GO), as its name implies, contains an abundance of oxygen functionalities and, indeed, many of the groups shown in Fig. 6.

As previously mentioned, the first production of LIG was based on the laser induced reduction of GO and thus it can be expected that the production of LIG directly from polyimide, while not free of oxygen groups, would nevertheless possess a smaller proportion. This has been confirmed by the work of Lin *et al.* (2014) where the at% oxygen as determined by XPS was found to decrease with the application of the laser and by Strong *et al.* (2012) who confirmed a decrease in C-O functionalities after laser reduction of GO using high resolution XPS analysis of the C 1s region. Again, it is important to recognize that the final form and composition will depend greatly on the characteristics of the laser configuration used, the production process parameters and post laser surface modification.

The ability to tune the LIG's hydrophilicity/hydrophobicity of the surface, exploit intrinsic defects and chemical functionalities and further enhance these native properties through the inclusion of exogenous catalytic, biological or other functional materials clearly opens up a vast array of possible applications. These include: supercapacitors (Li *et al.*, 2020a; Wang *et al.*, 2021) triboelectric nanogenerators (Stanford *et al.*, 2019; Zhao *et al.*, 2020), heaters (Chen *et al.*, 2020), rechargeable Zn-Air batteries (Ren *et al.*, 2019) and proton-exchange fuel cells (Tiliakos *et al.*, 2020).

LIG Based Sensors

In this review, the emphasis has been placed on the use of LIG based structures as the foundation for new smart devices for healthcare monitoring. This encompasses a large body of work and covers a diverse range of applications. Some of the more common areas within which LIG based devices have already been applied are highlighted in Fig. 7. The ability to monitor

Laser Induced Graphene Biomedical Sensors

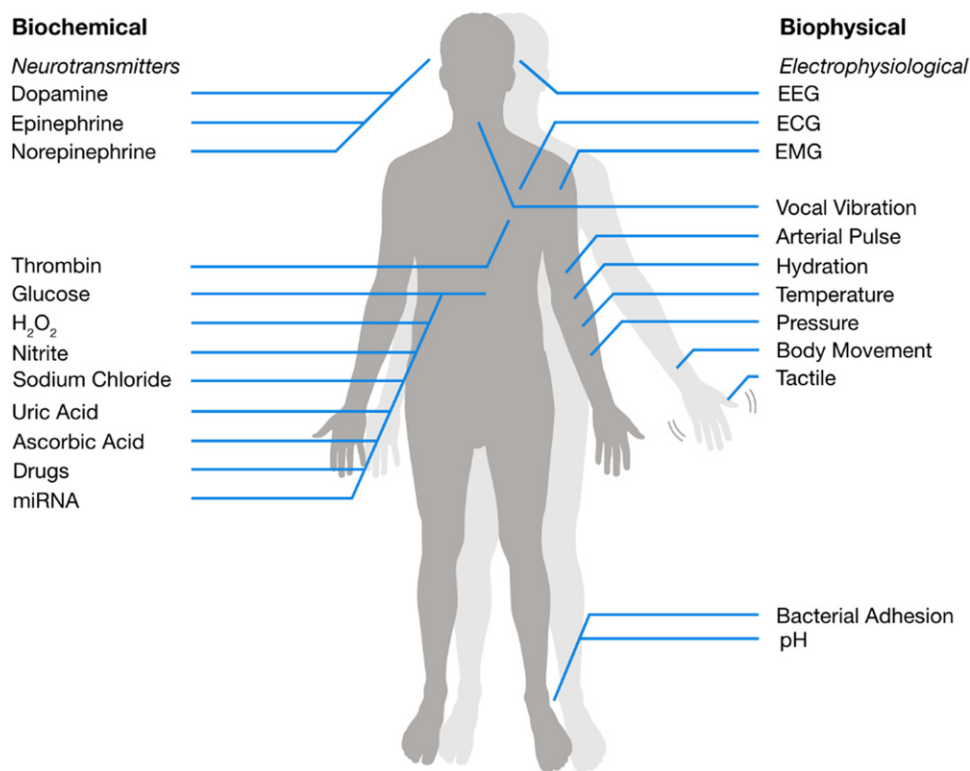


Fig. 7 Variety of sensing applications to which LIG is employed.

movement is an intrinsic feature of LIG and has stimulated substantial interest in the development of electronic skin, smart prosthetics and tactile sensors. The fast electron transfer kinetics available through the abundance of edge plane defect sites and the readily amendable modification of the surface with groups capable of providing selective interactions with key biomarkers has also brought LIG to the attention of the wider biosensing community. A critical overview of the various approaches to physical and biochemical monitoring is presented in turn in the following sections.

Physical Movement Monitoring

The skin is the largest organ of the human body and is often regarded as a protective barrier against the harshness of the environment within which the individual resides. It is a smart layer that not only provides a convenient elastic binder that enables movement, but one which helps to regulate the internal working of the body and protects the more delicate tissues from physical, chemical and microbiological insults. As such, the responsiveness and mechanical properties are clearly exceptional but beneath the physicality of the skin lies a supremely complex sensor network, which continuously monitors both physical and chemical stimuli. Pursuing the acquisition of electronic skin (e-skin) mimics, whether for prosthetics, robotics or for more general wearable technologies is inevitably challenging. While such developments remain far from the complex functionality of real skin, considerable gains have been achieved in recent years and some of these are summarized in [Table 2](#). It is little surprise that graphene and its various analogs have found application within the field given their mechanical, electrical and optical properties.

One of the basic functions of human skin is detecting physical force (tactile response) and mimicking this capability has been at the forefront of e-skin developments ([Wu et al., 2018](#); [Hosseindokht et al., 2020](#)). Human skin has characteristically low detection threshold, high spatial acuity, wide dynamic range and a fast response time. It is also described as an imperfect pressure detector providing a non-linear response, that enables subtle pressure and temperature changes to be detected at low ranges but not at higher ranges – especially when the two stimuli are combined ([Bae et al., 2018](#)). Previous electronic skin sensors have been centered around capacitance, triboelectricity and resistance. Resistance being favored among the three ([Zhu et al., 2018](#)). The heterogenous morphology of LIG based carbon structures renders the material susceptible to changes in electrical resistance, when subject to mechanical stresses. Far from being a limitation, this characteristic has been successfully exploited in the design of sensors for monitoring a variety of physical forces associated with common movements. A key example, in the form of stretchable strain sensor, is provided by the work of [Rahimi et al. \(2015\)](#) and illustrated in [Fig. 8](#).

Table 2 Application of LIG based substrates to the measurement of physical/vital signs

Analyte	Sample matrix	Comments	Laser Source	References
Electrocorticography	Rat brain tissue	N/A	CO ₂	(Lu <i>et al.</i> , 2016)
Temperature and Flow	Air / Water	20 μ m PDMS coating on flow sensor	CO ₂	(Marengo <i>et al.</i> , 2017)
Sound	Air	N/A	450 nm	(Tao <i>et al.</i> , 2017)
Movement, ECG, temperature, Hydration	Air / Skin	LIG / Sugar elastomer composite	CO ₂	(Sun <i>et al.</i> , 2018)
Body Movements	Air / Skin	LIG / PDMS or Ecoflex™ composite	CO ₂	(Wu <i>et al.</i> , 2018)
Proximity	Air	Capacitance Change	UV	(Chen <i>et al.</i> , 2019)
Body Movements	Air / Water	Double sided electrode coated in PDMS	CO ₂	(Kaidarova <i>et al.</i> , 2019)
Temperature	Skin	N/A	1064 nm	(Gandla <i>et al.</i> , 2020)
Arterial Pulse Wave	Air	N/A	UV	(Carvalho <i>et al.</i> , 2018)
Humidity	Plant	LIG coated with GO dispersion	450 nm	(Lan <i>et al.</i> , 2020)
Humidity	Air	Microwave resonator /LIG integrated sensor	CO ₂	(Adhikari <i>et al.</i> , 2019)

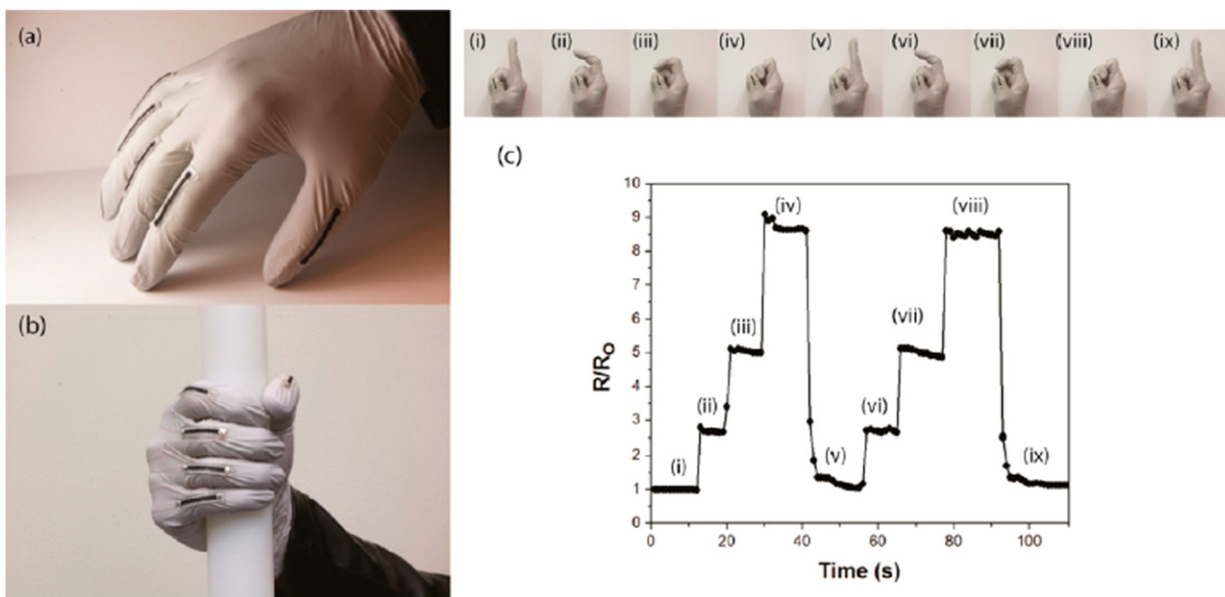


Fig. 8 Human finger motion detection with stretchable carbon traces. (a, b) Photograph of five stretchable strain sensors attached to the finger joints on the glove. (c) Relative resistance change of the strain sensors at different bending stages over time; the corresponding finger configuration for each plot region. Copyright (2015) American Chemical Society. Reprinted (adapted) with permission from Rahimi, R., Ochoa, M., Yu, W., Ziaie, B., 2015. Highly stretchable and sensitive unidirectional strain sensor via laser carbonization. *ACS Applied Materials and Interfaces* 7 (8), 4463–4470. Available at: <https://doi.org/10.1021/am509087u>.

Kaidarova *et al.* (2019) developed double-sided wearable sensors to measure the curvature and magnitude of applied forces. Their device demonstrated that resistance increased linearly with strain and had a gauge factor of ≈ 11.2 , comparable to that of commercial metallic strain gauges (Kaidarova *et al.*, 2019). The piezoelectric nature of LIG, whereby the change in pressure applied on the outside corresponds to a change in electrode resistance, lends itself for use as strain sensors in for electronic skin applications (Gong *et al.*, 2018; Chen and Yan, 2020). This resistance change is attributed to polarization of internal charges due to deformation and upon removal of the external force, the material rapidly returns to its uncharged state. Piezoelectric sensors provide a very fast response for dynamic pressure changes and are therefore well suited for pulsing signals. However, this detection mechanism struggles with static stimuli and therefore continuous monitoring of gradual pressure variations present a challenge (Liu *et al.*, 2019; Chen and Yan, 2020).

Ironically, the ability to measure changes in resistance as a consequence of movement can be irreversibly compromised by the very same action. As the underlying substrate (be it actual skin or a synthetic alternative) flexes with motion, the surface upon which the LIG rests will undergo a variety of forces (tension, compression and torsion), which can induce fracture or delamination of the actual sensing layer. Issues of stretchability are critical considerations in such cases, where the consequences of fracture cause circuit breaks and loss of response. As noted in the previous section, the flexibility of LIG can be rather contentious and, in many cases, the use of an in-fill polymer such as polydimethylsiloxane (PDMS) or Ecoflex™ can significantly improve the mechanical stability. Such procedures have been shown to result in very flexible and stretchable electrodes that are able to continue conducting under a 90-degree bending deformation, when used to record finger movements. Changing the bending radius of the sensor from flat to 10 mm, resulted in a resistance increase of 2000%, these devices were sustainable up to 70% with a gauge factor of 37 and pressure sensitivity of 0.088 K Pa⁻¹ (Wu *et al.*, 2018).

In addition, various approaches have been taken to address such issues and typically revolve around the use of refined design elements (serpentine, horse-shoe configurations and pre-strained elastomers / interconnects) and intrinsically stretchable materials (insulating and conductive). Conductive fillers (carbon nanotubes, conductive polymers and metal nanoparticles) are commonly used to facilitate conductive bridges between graphene fragments and provide network percolation even under strain and hence ensure retention of conductivity. In such cases, nanowires (i.e., silver) or nanotubes are favored as they possess an ability to form percolation junctions even at relatively low concentrations, which allows the bulk properties of the elastomeric skin mimic to be retained.

Vital Signs Monitoring

The conductive and flexible nature of LIG has also been considered as a possible substitute for conventional silver/silver chloride electrodes used in vital signs (ECG, EEG) monitoring (De Bacquer *et al.*, 1998). Prototype LIG electrodes have been shown to be capable of sufficient sensitivity to resolve the QRS complex in electrocardiograms with the raw signals possessing similar performance characteristics (signal to noise, amplitude etc) as the traditional Ag/AgCl systems. A core advantage, beyond the facile production of the electrodes, relates to the wearable acceptability of the electrodes given their inherent flexibility and absence of the conductive gel normally associated with Ag/AgCl electrodes (Sun *et al.*, 2018; Romero *et al.*, 2019). The inclusion of silver as a conductive interconnect (cf. previous section) between the graphenic components has also been exploited within this context for monitoring pulse, respiration, blink rate and wrist movement as well as further enhancing ECG and EEG performance (Qiao *et al.*, 2020). Some of the more successful designs are summarized in Table 2.

Thermoacoustic Sensors

Thermoacoustic sensors based on LIG have been exploited to detect and generate sound for the creation of artificial throat. In such cases, the intention has been to convert or parse nonword / paralinguistic sounds (i.e., hum, cough, scream) to something that has recognizable meaning (Tao *et al.*, 2017; Wei *et al.*, 2019). The implications are clearly tremendous for those suffering with a damaged or malfunctioning larynx (as a result of cancer, stroke or genetic anomaly). The high thermal conductivity and low heat capacity of the LIG substrate can be exploited since that the application of an appropriate AC voltage enables the rapid resistive heating. The latter has been used to considerable effect in some sensing applications (see later) but in this context is responsible for heating the surrounding air, whose expansion results in a sound wave. The LIG vocal “cords” were found to produce sounds with frequency of 100 Hz to 40 kHz. The vibration of these cause a change in resistance (and hence a fluctuation in current), which allows the device to function as both sensor and actuator and has been shown to differentiate between a variety of nonword sounds (at variable tone and volume). It therefore has the potential for voice recognition and, in combination with appropriate algorithms, it has been suggested that it could generate specific volume/frequency sound (and hence words) from detecting the initial hum of the patient (Tao *et al.*, 2017; Wei *et al.*, 2019).

Chemical Sensors

Carbon has served as the foundation of countless sensors – irrespective of end application – and has been the mainstay of commercial home glucose monitoring for several decades. Electrodes can take a multitude of forms from carbon felts through to impervious diamond and can be tuned and tailored to a particular application in terms of both performance and cost. Screen printed carbon electrodes (SPCEs) have unquestionably been a revelation for the development of point of care diagnostics whether aspirational or those that finally reached commercial maturity. The ability to pattern the carbon into large numbers of low cost electrode assemblies, which could be used as a disposable sensing platform deftly overcame the issues of reproducibility that had previously dogged the more expensive substrates such as platinum, gold and, indeed, other forms of carbon. The availability of graphene (and graphene oxide) and their inclusion onto solid substrates met with similar problems of providing intra and inter electrode repeatability. The evolution of LIG based electrodes in contrast, offered an alternative to the SPCE systems – providing the ability to rapidly produce (and modify) electrode configurations at volume without the expense of custom meshes and conductive inks. LIG based electrodes also possessed a crucial advantage over the SPCE systems in that their native electrochemical performance is, in many respects, superior to the graphite commonly employed in the commercial inks. Historically, edge plane pyrolytic graphite (EPPG) has been the “gold standard” for carbon materials in electrochemical assays due to the availability of large number of defect sites at the edge planes (Banks and Compton, 2006). Burke *et al.* demonstrated LIG possessed a HET rate, calculated with the Nicholson method of $(13 \pm 1) \times 10^{-3}$ cm/s, this is similar to the ‘gold standard’ EPPG ($= 8.8 \times 10^{-3}$ cm/s) (Burke *et al.*, 2020). The breadth of analytes to which LIG based sensors have been applied are detailed in Table 3.

The systems highlighted in Table 3 are based on direct electron transfer (the majority being oxidation electrode processes) between the target analyte and the LIG substrate. The electroanalytical capabilities of the LIG based system have been successfully demonstrated through the resolution of ascorbate, urate and dopamine processes – a classic three redox probe system, which usually results in highly ambiguous/overlapping peak processes on conventional carbon surfaces (Nayak *et al.*, 2016; Hong *et al.*, 2018; Xu *et al.*, 2018a,b; Hui *et al.*, 2019; Muralidharan *et al.*, 2020). In a few instances, catalytic materials added to the LIG aid in the electroanalytical detection (Li *et al.*, 2020b; Zhang *et al.*, 2020). It is noteworthy that in some cases the LIG is transferred from the polyimide to a secondary, more flexible substrate to improve the robustness of the system (Rahimi *et al.*, 2017; Hui *et al.*, 2019; Yoon *et al.*, 2019; Muralidharan *et al.*, 2020; Prabhakaran and Nayak, 2020). The use of poly(4-ethylenedioxythiophene) (PEDOT) is also notable for serving as a conductive network/interconnect.

Table 3 Application of LIG based chemosensors

Analyte	Sample	Comments	Laser Source	References
Ascorbate, Dopamine, Urate	Buffer	PEDOT modified LIG. DPV detection.	CO ₂	(Xu <i>et al.</i> , 2018a)
Dopamine, Epinephrine, Norepinephrine	Human urine	Grass-like laser-scribed graphene on polyimide. DPV detection.	CO ₂	(Xu <i>et al.</i> , 2018b)
Ascorbate, Dopamine, Urate	Buffer	Polyimide coating on ITO glass. DPV detection.	CO ₂	(Hong <i>et al.</i> , 2018)
Dopamine	Human urine	Au-Pt nps on LIG transferred from Polyimide to PDMS. DPV detection.	CO ₂	(Hui <i>et al.</i> , 2019)
Dopamine	Artificial sweat	Cu(II) treated LIG and graphene ink integrated sensor. CV detection.	CO ₂	(Muralidharan <i>et al.</i> , 2020)
Urate, Tyrosine	Sweat	LIG multielectrode array for simultaneous sweat sampling, chemical sensing and vital-sign monitoring. DPV detection of urate & tyrosine.	CO ₂	(Yang <i>et al.</i> , 2020)
Ascorbate, Dopamine, Urate	Buffer	Pt nanoparticles. DPV detection.	CO ₂	(Nayak <i>et al.</i> , 2016)
pH	Buffer	Riboflavin redox probe adsorbed onto LIG. SWV detection.	CO ₂	(Barber <i>et al.</i> , 2021)
pH	Simulated wound tissue	Serpentine LIG design on polyimide plasma bonded to Ecoflex™. PANI pH receptor with potentiometric detection.	CO ₂	(Rahimi <i>et al.</i> , 2017)
Cellular activity	Adherent cells in media	Qualitative impedance based monitoring of cell growth.	CO ₂	(Puetz <i>et al.</i> , 2020)
Hydrogen Peroxide	Buffer	LIG transferred to Au electrode by soluble tape. Au-LIG substrate further modified by Pt nps. Amperometric detection + 0.4 V.	CO ₂	(Yoon <i>et al.</i> , 2019)
Hydrogen Peroxide	Buffer	Multielectrode array. CV detection.	CO ₂	(Kothuru <i>et al.</i> , 2020)
Glucose (non enzyme)	0.1M KOH	Polyethersulfone (PES) polymer. CdS / Ni photoelectrode detection.	CO ₂	(Li <i>et al.</i> , 2020b)
Glucose (non enzyme)	0.1M NaOH	Cu Nanocubes. Amperometric detection + 0.55 V. Kapton tape on PVC sheet.	400–450 nm	(Tehrani and Bavarian, 2016)
Glucose (non enzyme)	Human serum and sweat	Ni decorated carbon paper substrate. Amperometric detection + 0.5 V.	450 nm	(Hou <i>et al.</i> , 2019)
Glucose (non enzyme)	Blood, serum and sweat 0.1M NaOH	LIG transferred from Polyimide film to Scotch tape. CuO nps. Amperometric detection + 0.4 V.	CO ₂	(Prabhakaran and Nayak, 2020)
Glucose (non enzyme)	Blood serum 0.1M NaOH	Zinc foil connected to LIG layer for substrate-assisted electroless deposition (SAED) of Cu nps. Amperometric detection + 0.5 V.	NS	(Zhang <i>et al.</i> , 2020)

Where: ENZ = Enzyme; APT = Aptamer; Ab = Antibody; MIP = Molecularly imprinted polymer; nps = nanoparticles; N/S = not specified; EIS = Electrochemical impedance spectroscopy; DPV = Differential pulse voltammetry; SWV = Square wave voltammetry; CV = Cyclic voltammetry; PEDOT = Poly(3,4-ethylenedioxythiophene); PANI = Polyaniline; PDMS = polydimethylsiloxane.

A wide variety of analytes are highlighted in **Table 3** but the actual implementation of LIG based sensors in real world contexts can be questionable. A key example is the large number of non enzymatic glucose sensors and while there is certainly considerable interest in flexible sensors (patches, tattoos etc) for diabetes monitoring, the examples shown have very limited applicability for direct in situ analysis given the requirement for extreme alkaline conditions (the skin would not be particularly accommodating to 0.1 M NaOH). Likewise, the use of ascorbate, dopamine, urate present more of a function in terms of highlighting the resolution capabilities of the LIG based system rather than there being a clear end product/sensor.

The measurement of pH using LIG however stands in contrast to the other targets in **Table 3** in that it is arguably among the more appropriate uses of the novel material especially for biomedical applications, where it is possible to capitalize fully on its ease of fabrication, flexibility, scalability and hence disposability. It is also significant in terms of the increasing sophistication of the fitness tracker devices where there is a requirement for more holistic information on the bodily function. The chemical analysis of sweat by such devices is undoubtedly the next stage in the evolution of such devices.

Healthy skin is usually considered to possess an “acid mantle” in which the surface maintains a slight acidic pH (typically pH 4 to pH 6) in order to function as an effective impediment to the proliferation of skin flora and potential pathogens. It is little surprise, that pH has a substantial influence on the biochemical reactions taking place on the skin but also within the tissues (Schneider *et al.*, 2007) and hence has a critical role in pathogenesis of skin diseases such as: acne vulgaris, ichthyosis and Candida albicans infections (Zahed *et al.*, 2020). In general, bacteria colonize and thrive under more alkaline conditions and this can prove particularly problematic where the skin is wounded. The underlying tissues and blood will typically have a pH of around 7.4 which is a more welcoming environment for bacterial growth. The use of visual indicator papers or the traditional glass pH electrode is not suitable in such contexts and this has

sparked considerable interest in the development of new pH monitoring strategies suitable for providing quantitative measures on skin or wound pH while being both disposable and inexpensive (Alam *et al.*, 2018; Salvo *et al.*, 2018).

The combination of LIG flakes sprayed with Poly(3,4-ethylenedioxythiophene) / poly(styrene sulfonate) (PEDOT:PSS) which, as mentioned previously, serves as an interconnecting conductive network – especially where mechanical flexing of the sensor occurs. The additional functionalization with polyaniline (PANI) confers pH sensitivity to the composite and was shown to provide a super Nernstian potentiometric response of 75 mV/pH over pH 4 to pH 7 (Zahed *et al.*, 2020). An alternative approach involving PANI exploited a serpentine design to overcome the fragility of the LIG to strain and was based on a LIG-Ecoflex™ combination. A near Nernstian response of 53 mV/pH was observed but the critical feature here was the ability to withstand elongations of 135% and is clearly of benefit in dermal or wound tissue applications, where mechanical movements in the underlying or surrounding skin are likely (Rahimi *et al.*, 2017). Voltammetric approaches to pH measurement have become common but few have yet to make the transfer to LIG based substrates. One exception, exploits the pH dependent redox properties of Riboflavin (vitamin B2) to serve as inherently biocompatible marker for pH. The oxidation peak position of the riboflavin shifts with pH (59 mV/pH) and, in contrast to the potentiometric systems, provides rapid, drift free assessments. The adsorption of the riboflavin onto the LIG surface also opens the door towards reagentless sensing applications (Barber *et al.*, 2021).

LIG Based Biosensors

The direct electrochemical detection of target biomarkers is rather limited to small molecular weight targets and while their detection in solutions of limited composition can give rise to impressive detection limits, the acquisition of selectivity in more complex media can be challenging. The responses obtained at LIG electrodes can aid resolution but it is not universally effective and, as such, more elaborate approaches are often required – especially when attempting to detect large macromolecular species that perhaps have no intrinsic or easily accessible redox properties. A summary of the various detection methodologies shown in Fig. 9 where the evolution of direct analysis (A) lead to the use of enzyme systems (B) and, more recently to antibody/aptamer (C) approaches.

The electrochemical detection of hydrogen peroxide, a principal by-product of oxidase enzyme reactions (Xuan *et al.*, 2018; Yoon *et al.*, 2020; Zahed *et al.*, 2020), sits at the heart of many of the enzyme systems described in Table 4. It is also a biomarker in its own right (hence its inclusion within Table 3) where it is recognized as both an intracellular signalling and, in situations where there is an excess of reactive oxygen species, a cytotoxic agent (Giorgio *et al.*, 2007; Tehrani and Bavarian, 2016; Kim *et al.*, 2018; Prabhakaran and Nayak, 2020; Zhang *et al.*, 2020). It is little surprise, that there is an extensive literature base on the detection of H_2O_2 with graphene based materials featuring prominently in recent years with detection limits as low as 27.7 pM and 0.2 nM for enzymatic and non-enzymatic approaches respectively (Dinesh *et al.*, 2014; Liu *et al.*, 2014; Zhang and Chen, 2017). The decoration of the LIG foam with noble metal nanoparticles (typically Pt or Au) has also demonstrated considerable activity towards peroxide (Malekzad *et al.*, 2017; Yoon *et al.*, 2019; Kothuru *et al.*, 2020). In contrast to the non enzymatic glucose sensors described in Table 3, those based on Glucose Oxidase can function at physiological pH, and exploit the supreme selectivity of the enzyme, providing more accurate response – a prerequisite for effective diabetes management.

The detection of protein biomarkers, which are more commonly associated with disease and injury, represent a far greater challenge to electrochemical sensors and requires a different detection strategy. Selectivity towards particular targets requires the use of an appropriate antibody (or aptamer) but, in contrast to the enzyme systems listed in Table 4, the difficulty arises in attempting to determine when the target (antigen) has not only bound to the antibody but how much has bound. There have been numerous approaches to the design of electrochemical immunosensors and a detailed discussion of each is beyond the scope of the present review.

It is notable that in those approaches employing aptamers and antibodies, label free strategies predominate (Fig. 9(C)). The use of impedimetric (and capacitance) analysis is arguably the simplest detection methodology and has been applied to a wide selection of targets (from proteins to living cells). The ability to scribe LIG interdigitated electrodes has been widely used for supercapacitor

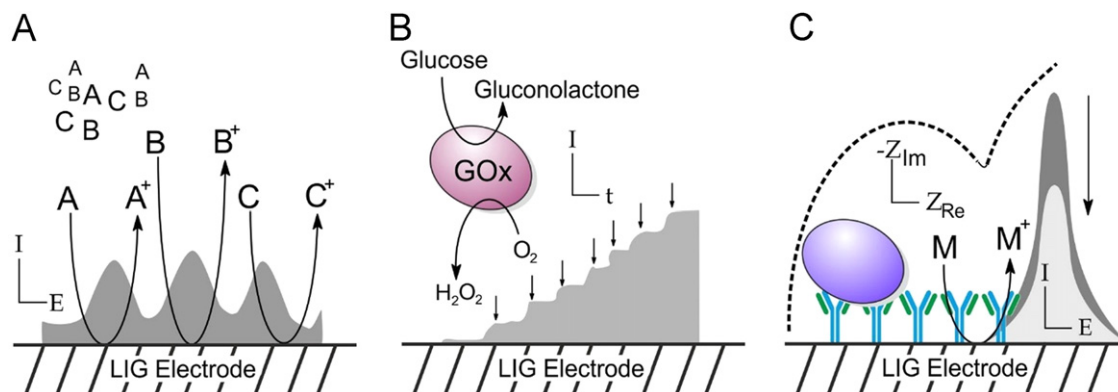


Fig. 9 Electroanalytical detection methodologies. (A) Direct oxidation/reduction. (B) Enzymatic/ampereometric detection. (C) Antibody/Aptamer detection via voltammetric or impedance techniques.

Table 4 Application of LIG based biosensors incorporating enzymes, aptamers, antibodies or molecularly imprinted polymer systems

Analyte	Sample	Type	Comments	Laser source	References
Histamine in Food	Fish paste	ENZ	Diamine Oxidase, Cu nps Amperometric detection + 0.5 V.	405 nm	(Vanegas <i>et al.</i> , 2018)
Acetylcholinesterase inhibitors	N/S	ENZ	Acetylcholinesterase immobilised on TiO ₂ /LIG/ITO photoelectrode. Amperometric / photocurrent.	CO ₂	(Ge <i>et al.</i> , 2019)
Glucose & pH	Sweat	ENZ / PANI	Glucose Oxidase immobilised with Pt/Au nps on LIG/Ag nanocomposite on PDMS. Amperometric / potentiometric detection.	CO ₂	(Xuan <i>et al.</i> , 2018)
Glucose	Sweat	ENZ	Glucose Oxidase immobilised with electrodeposited Pt nps on LIG. Amperometric detection + 0.45 V.	CO ₂	(Yoon <i>et al.</i> , 2020)
Glucose / H ₂ O ₂	Sweat	ENZ	Controlled surface wettability of the LIG surface. Immobilised Glucose Oxidase. Amperometric detection – 0.1 V.	1064 nm	(Li <i>et al.</i> , 2019)
Urea /pH	N/S	ENZ	Chitosan-Urease. pH measured by potentiometry and visual indicator paper.	CO ₂	(Mamleyev <i>et al.</i> , 2019)
Thrombin	Fetal calf serum	APT	Capacitance based sensing based on interdigitated LIG electrodes.	CO ₂	(Yagati <i>et al.</i> , 2020)
Thrombin	Fetal calf serum	APT	Label Free ferrocyanide redox probe. DPV detection.	CO ₂	(Fenzl <i>et al.</i> , 2017)
Ascorbate, Amoxicillin	N/S	MIP	PEDOT/4-Aminophenol electropolymerized on LIG. SWV detection.	CO ₂	(Marques <i>et al.</i> , 2020)
Chloramphenicol	Buffer	MIP	Electropolymerization of Eriochrome Black T onto LIG. EIS detection.	CO ₂	(Cardoso <i>et al.</i> , 2019)
Bisphenol A	River water	APT	ac electroosmotic based capacitance sensing of Bisphenol A-APT binding.	1030 nm 532 nm	(Cheng <i>et al.</i> , 2016)
Salmonella	Chicken broth	Ab	Label free EIS detection.	CO ₂	(Soares <i>et al.</i> , 2020)
<i>E.coli</i>	N/S	Ab	Metal nps chitosan coated onto LIG. EIS detection.	N/S	(You <i>et al.</i> , 2020)
miRNA	N/S	miRNA	Label free ferrocyanide redox probe. DPV detection.	CO ₂	(Wan <i>et al.</i> , 2020)
SARS-CoV-2 antigen, antibodies and CRP	Blood and Saliva	Ab	Multiplexed detection of disease antigen/antibodies/severity biomarker. Amperometric detection.	CO ₂	(Torrente-Rodríguez <i>et al.</i> , 2020)

Where: ENZ = enzyme; APT = Aptamer; Ab = Antibody; MIP = Molecularly Imprinted polymer; nps = nanoparticles; N/S = not specified; EIS = Electrochemical Impedance Spectroscopy; DPV = Differential Pulse Voltammetry; SWV = Square wave voltammetry; PEDOT = Poly(3,4-ethylenedioxythiophene); PANI = Polyaniline; PDMS = Polydimethylsiloxane.

studies but it is clear from **Table 4** that such approaches can equally be of value to sensing applications. The use of voltammetric systems (typically differential pulse or square wave) have also been assessed and rely on the bulk of the antibody or aptamer bound target impeding the access of a redox probe (typically ferrocyanide). Soares *et al.* (2020) found that by using LIG as an electrode base material for the functionalized antibodies, the sensor achieved a detection limit of 13 ± 7 CFU mL⁻¹ using EIS (Soares *et al.*, 2020). This is a significant improvement on earlier work by Farka *et al.* (2016), who used a modified gold SPE in a similar detection method and analysis time, which demonstrated a larger detection limit of 10^3 CFU mL⁻¹ (Farka *et al.*, 2016). The electrochemical properties of LIG appears to have aided in overcoming detection limit shortcomings, confirming LIG's value within immunosensor applications (Soares *et al.*, 2020). The use of LIG to serve as a foundation for molecularly imprinted polymer (MIP) templates has also been demonstrated and essentially adopted similar detection strategies to those used in the other affinity receptors.

Recently LIG was used for the development of an impedimetric immunosensor, based on the modification of the LIG surface with antibodies for the detection of *S. enterica* bacterium (Soares *et al.*, 2020). Although this method was primarily for the detection of Salmonella within the food industry, if directed towards the medical sector, it is envisaged that the generic nature of the underpinning methodology could be applied to other targets (Barreiros dos Santos *et al.*, 2015; Sheikhzadeh *et al.*, 2016). Currently, pathogen detection consists of polymerase chain reaction experiments or bacteria plate counting, which not only entails expensive lab equipment but is time-consuming due to the pre-enrichment steps required (Clais *et al.*, 2015). One of the primary hurdles associated with biosensing applications is the poor detection limits (Soares *et al.*, 2020). To improve this, many researchers integrate a preconcentration step, however this does not speed up the testing time, querying its classification of a "rapid" sensor (Soares *et al.*, 2020).

Electrochemical biosensors have applications in rapid POC testing for infectious disease as the detection mechanism does not require the isolation and purification protocols used in RT-PCR assays. A multiplexed LIG sensor, the SARS-CoV-2 RapidPlex employs covalently tethered capture antibodies and proteins to quantitatively detect SARS-CoV-2 nucleocapsid protein and specific antibodies respectively in human serum (Torrente-Rodríguez *et al.*, 2020). To further increase the merit of their sensor, the researchers integrated a sandwich assay electrode for the quantification of C-reactive protein (CRP) to provide users with an indicator of disease severity and influence clinical management. The researchers report a significant increase in the amperometric signal after just 1 min of incubation in the target analyte and achieved a linear correlation with results using a standard ELISA.

Graphene's Antifouling and Antibacterial Properties

Bacterial contamination of medical devices and the complications that arise from any subsequent infection have led to extensive investigations into the antimicrobial coatings. While early attempts focused on the use of antibiotics (Pandey *et al.*, 2011), the increasing rise of antimicrobial resistance (AMR) has prompted urgent search for alternatives (Chovanová *et al.*, 2013). Metal nanoparticles (typically silver) have been investigated but there are concerns over their efficacy and biocompatibility, where leaching can occur (Yeaman and Yount, 2003; Liu *et al.*, 2008; Ahamed *et al.*, 2010). Antimicrobial peptides bearing biguanide functionalities are a more recent development where the latter interfere with the cell wall of the microbe and, when covalently tethered to the device substrate, promoting a contact kill mechanism (Wang *et al.*, 2014). Graphene and its analogs, similarly, have been shown to interact with the cell membrane but, the oxidized graphene in particular, can also serve as a redox cyclor promoting the generation of intra-cellular reactive oxygen species (ROS), which can prove cytotoxic to the organism.

Contact angle examination of LIG reveals that the surface possesses a more hydrophilic structure than either graphite or PI (Ye *et al.*, 2018b) and, as such, reduces the propensity of hydrophobic components from adsorbing to the surface that, in turn, impedes bacterial adhesion (Al-Juboori and Yusaf, 2012). LIG also has a negative zeta potential (-44.4 mV) and as that *P. aeruginosa* is similarly negative (-23.3 mV), it is believed the electrostatic repulsion also helps to inhibit bacterial attachment (Singh *et al.*, 2017). As graphite and polyimide have a higher negative potential ($-X$ and $-Y$ mV respectively), it has been suggested that they are more prone to electrode fouling hence susceptible to biofilm adherence (Bernstein *et al.*, 2014).

A more active approach can be employed, whereby the imposition of a potential at the electrode can dramatically increase graphene's antibacterial capabilities (Singh *et al.*, 2017). Studies of LIG have shown that the application of a voltage of between $+1.5$ and $+2.5$ V was effective in removing bacterium from a solution with over 99% of bacteria destroyed in the first four hours (Singh *et al.*, 2017; Ye *et al.*, 2018b). In contrast, solutions left at open circuit had little or no effect on the bacteria. It is thought electrostatic migration of the negatively charged *P. aeruginosa* to the anode exposes them to the higher levels of active chemical species near the electrode (Liu *et al.*, 1997), whilst also forcing them closer to the graphene by the electric field distributed from the electrode. It has been suggested that the bacteria are subjected to irreversible electroporation (or electron transfer) (Singh *et al.*, 2017; Kumar *et al.*, 2019) with nanopores in the cell membrane disrupting homeostasis and ultimately causing cell death. This is believed to be the main property of graphene's "toxicity" as the bacterium can no longer reproduce due to the repetitive oxidative stress (Akhavan and Ghaderi, 2010; Perreault *et al.*, 2015).

Graphene's morphology also contributes to the decontamination rate, with most cellular damage caused by its sharp edges that can pierce the bacterium (Kumar *et al.*, 2019) as it is pulled by the electric field across the rough surface (Singh *et al.*, 2017), causing leakages of the intracellular matrix (Akhavan and Ghaderi, 2010) and cell deformation (Perreault *et al.*, 2015). Alongside this, the large surface area intrinsic to graphene nanoflakes and foams help to increase the current produced and, even at low voltages, can improve the electrochemical processes, again contributing to its antifouling abilities (Singh *et al.*, 2017).

At present, graphene's antibacterial attributions, with reduced toxicity, have allowed it to be used with antibacterial enzymes and antibiotics in drug delivery systems (Kumar *et al.*, 2019). Huang *et al.* (2020) showed that LIG demonstrates superior bactericidal properties compared to other filtering layers used in commercial facemasks (Huang *et al.*, 2020). A layer of LIG achieved an 81.57% decrease in *E. coli* CFU after 8 h, a significant improvement on the 9.13% decrease yielded by the melt-blown fabric used in surgical masks. This bactericidal activity was shown to be expedited by the photothermal effect, increasing to 99.84% after 5 min in sunlight. Its formation has also allowed LIG to be produced onto lignocellulose materials, meaning it can be transferred onto biodegradable devices (Ye *et al.*, 2018b). For the future, there is potential for LIG's antibacterial properties to be exploited for use in smart bandages to increase healing within infected wounds, help destroy antibiotic resistant bacteria and control the growth rate of cancer cells (Shahnawaz Khan *et al.*, 2015).

Overall, graphene exhibits great antifouling and antibacterial qualities, however it is feasible to take into account the type and shape of bacterium will ultimately affect graphene's antibacterial efficiency (Kumar *et al.*, 2019). Nevertheless, graphene's distinctive structure and chemical properties creates new opportunities for LIG to be used as a coating for antibiofilm devices, due to its adverse environment for bacterial growth or attachment (Singh *et al.*, 2017).

Biocompatibility of Graphene/LIG Structures

At present, there are multiple studies, outlining graphene's toxic effects with animal and human cells (Kumar *et al.*, 2019), which pose a problem for possible medical applications. To assess graphene's biocompatibility with the human body, we need to understand the mechanisms that facilitate bacterial death. Currently there are many reasons considered, as mentioned in Section "Graphene's Antifouling and Antibacterial Properties". However, the involvement of different factors means the actual mechanism is not fully apparent. Nonetheless, from the information studied so far, if graphene can affect the cell of a bacterium, it is likely it could affect human cells in the same manner.

Graphene interacts with single stranded DNA more than double-stranded or tertiary DNA structures, through π - π stacking and hydrophobic forces (Kumar *et al.*, 2019). Single stranded DNA is important in DNA synthesis, genomic stability, repair and maintenance (Wu *et al.*, 2016), thus, if graphene affects any of these processes a disruption in homeostasis could occur. A study conducted by Tan *et al.* (2013) found graphene lowered serum protein binding, whilst activating Complement Component 3(C3), known to damage the membranes of cells (Tan *et al.*, 2013). While another study conducted by Gan *et al.* (2015) demonstrated

that graphene, through π - π relations, was bound with blood proteins (Gan *et al.*, 2015). If the internal components of the human body are in contact with graphene (this could be applicable to drug delivery or wound monitoring devices) there is a probability that GBM, including LIG, will affect human cells similarly to bacteria.

It should be highlighted that carbon is well known for its toxicity, and as graphene is a single layer of carbon (Akhavan and Ghaderi, 2010), there are worries about the health risks of graphene being implemented into biomedical devices. Joint toxicity should also be noted, especially in regards to graphene-based materials (Kumar *et al.*, 2019). This is linked to the synergetic effect of graphene paired with other materials, which in turn can affect the toxicity of the product developed. There is a significant number of studies focusing on graphene toxicity but due to discrepancies in results, along with a lack of global acceptance criteria, this toxicity is still being debated (Kumar *et al.*, 2019). Hu *et al.* (2011) found the main cause of cytotoxicity was caused by the direct interaction between cell membranes and graphene that resulted in physical damage to the membrane (Hu *et al.*, 2011). This was likely caused by graphene's sharp edges due to its honey-comb structure (cf. its antibacterial action). In a different study, Liao *et al.* (2011) stated that graphene was linked to cytotoxicity in human skin fibroblasts and erythrocytes. In this study, it was discovered that the graphene's surface oxygen content, charge, state and particle size all affected the biological response (Liao *et al.*, 2011). Most information points to the contact time of graphene with cells, along with its concentration, as the main variables to toxicity, and thus by increasing these parameters, the cells functionality will decrease (Kumar *et al.*, 2019). This is clearly a potential problem when it comes to graphene's use in biomedical applications if the material is in contact with open wounds, surgical wound entries for catheters or placed it in direct contact with human cells.

The in vivo biocompatibility of LIG derived from polyimide has been assessed with a zebrafish embryo model (d'Amora *et al.*, 2020). The homology between human and zebra fish was been confirmed with genomic sequencing suggesting sufficient similarity. This model has been proven to be an excellent indicator for rodent toxicity (Ali *et al.*, 2011). Zebra fish embryos were then either injected or soaked in different concentrations of LIG dispersed in water at various stages in development. The typical health indicators, heart rate, morphology and swimming activity were subsequently examined to evaluate the biocompatibility. It was found that even high concentrations of LIG did not interfere with embryo development and no toxic effects were observed. This is particularly encouraging as pristine graphene significantly affected the survival and morphology using the same assay (Manjunatha *et al.*, 2018). Extrapolating this conclusion of biocompatibility to mammals should be done with caution as further investigation of the material used in bulk as a tissue interfaced electrode is required.

Another aspect to take into account is the bacterial tests carried out in many studies which focus directly on *P. aeruginosa*, *S. aureus* and *E. coli* (Kumar *et al.*, 2019) meaning it is not clear how graphene affects all types of bacteria. More research is required into extensive antibacterial tests to identify which bacteria are affected by graphene. It is important to gather as much information from this as possible due to the ongoing threat of antibiotic resistant bacteria in the future. This could also help distinguish the mechanism that causes the bacteria to breakdown.

Aside from the concerning biological response, an ongoing issue is the lack of quality control in manufacturing the graphene family of materials, including LIG. Many manufacturing techniques lack controllable, inexpensive and manageable methods to produce high quality graphene (Yu *et al.*, 2017), hence a set criteria will need to be established for manufacturers enabling these materials to be available for commercial use in a medical setting. Graphene quality is typically only assessed by the number of layers present, however, as there are no set standards, a material with a structure more similar to graphite could be mistakenly described as graphene (Kauling *et al.*, 2018). Many researchers believe this issue needs to be addressed as it is vital for graphene's intrinsic properties to be preserved and its stabilization of single or few-layer graphene sheets (Kauling *et al.*, 2018).

According to Kauling *et al.* (2018) graphite can produce completely different results to graphene and could therefore not be as efficient in sensing mechanisms (Kauling *et al.*, 2018). This creates a problem as a sensor's main characteristic is to provide highly accurate and precise readings. If there is no set standard for the quality of graphene, this could produce a variation of readings or results meaning a sensing device could essentially be inconsistent. This problem alone could limit the role of graphene in biomedical applications considering the high standards medical devices need to pass before being used commercially. Consequently, the reproducible quality of graphene needs to be further researched and improved upon, especially in high precision sensing technologies (Kauling *et al.*, 2018).

Conclusions

In the few years since its first description, laser induced graphene has demonstrated a comparable boom in research interest to its impactful graphene predecessor. The ability to simultaneously manufacture and pattern a common, insulating substrate with commercial laser systems provides the GBM family with previously lacking fabrication control and therefore batch to batch repeatability. The versatility of the material has been unlocked by varying the composition of the substrate, laser parameters and any number of post processing steps. A combination of unique physical characteristics including high porosity, conductivity and density of electron rich defects bestow the material with ideal properties for application to wearable healthcare devices. This has been demonstrated with a number of physical and biochemical flexible sensors, which, subject to validation and demonstration of biocompatibility could lead the way towards more functional / wearable sensors and a more holistic connected health system.

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Effects of Doping/Co-Doping on $\text{Li}_2\text{FeSiO}_4$ Cathode Material for Lithium-Ion Batteries: A Review

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Abstract

$\text{Li}_2\text{FeSiO}_4$ has drawn attention recently as a cathode material due to its convincing features like the optimal working voltage, low toxicity, high theoretical capacity, high security, environmental friendliness, high elemental abundance, and low cost. However, this olivine structured $\text{Li}_2\text{FeSiO}_4$ may cause low electronic conductivity and lithium-ion diffusion coefficient, which limits its electrochemical performance. Therefore, many efforts have been made recently to overcome these challenges and to enhance the electrochemical performance of the $\text{Li}_2\text{FeSiO}_4$ cathode. The proper cation substitution on the Fe-site and Si-site can facilitate the easy migration of lithium-ion in the diffusion channels which results in increased intrinsic electronic conductivity. Thus, the single or multi-elements doping method would be a useful technique to improve the electrochemical properties of $\text{Li}_2\text{FeSiO}_4$. This article highlights the various doping effects on $\text{Li}_2\text{FeSiO}_4$ cathode material for lithium-ion batteries.

Key Points

- This article reviews the development of orthosilicates-based cathode materials, especially $\text{Li}_2\text{FeSiO}_4$, in lithium-ion batteries (LIBs).
- Types of dopants used and their effect on structural and electrochemical properties of $\text{Li}_2\text{FeSiO}_4$ -based LIBs.
- Provide important status updates of the co-doped materials and electrochemical properties.
- An overview of challenges encountered and future directions of existing orthosilicates-based cathode materials.

Introduction

The world's energy consumption has been increasing exponentially throughout the last few decades, along with CO_2 emission (Meinshausen *et al.*, 2009). Long-term fossil fuel consumption has given rise to some serious issues like environmental pollution and global warming. Thus, immediate development of clean and renewable energy sources like solar cells, fuel cells, batteries, waves, wind power generators, etc., are necessary to reduce the devastating effects of global warming. Among all these renewable energy sources, rechargeable batteries are one of the best sources that serve the purpose to replace fossil fuels. Lithium-ion battery (LIB) can effectively store energy in the form of chemical energy and has become the primary power source of portable products due to its high energy density, long cycle life, and low cost (Yi *et al.*, 2020). From 2014–2019, its application in electric vehicles (EVs), hybrid electric vehicles (HEVs), smart grids, portable electronic devices has doubled (Boyden *et al.*, 2016). To meet the high expectation, the development of high specific capacity lithium-ion batteries has received significant attention. However, no significant development of the capacity of a lithium-ion battery has been noticed in the last decade, and this can largely be attributed to the lacking of discovery of a cathode material with high specific capacity. Therefore, research and development of lithium-ion batteries are mostly concentrated now on enhancing the capacity of cathode material which is holding down the immense promise of this alternative energy source.

The early cathode materials such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , LiMnO_2 , etc., have some limitations in their applications due to high cost, toxicity issues, inherent chemical and thermal instability. In search of something convenient, a new group of polyoxyanion cathodes based on the orthosilicates (Li_2MSiO_4 , where $\text{M}=\text{Fe}$, Mn , and Co) has been drawn the attention due to their strong Si–O bonds, abundance, and lowest cost. Indeed, developing cheap, sustainable, and safe cathode materials is a prime target for large-scale lithium batteries. A key feature of the Li_2MSiO_4 system is that, in principle, extraction of two lithium ions is possible for a two-electron redox process (i.e., operating on both $\text{M}^{2+}/\text{M}^{3+}$ and $\text{M}^{3+}/\text{M}^{4+}$ redox couples); this feature produces a higher capacity (e.g., above 300 mAh g^{-1} for Li_2MSiO_4). Supervalent cation doping has rarely been attempted for orthosilicate materials until now. This review paper aims to critically analyze the effects of doping on lithium-iron silicate cathode and provide an overview of the growing area of new cathode materials for lithium-ion batteries.

Rechargeable Battery Systems

A battery can reduce environmental pollution and global warming caused by conventional energy sources, such as coal and fossil fuel. Moreover, batteries can directly convert the chemical energy stored into electricity without any moving parts or noise pollution. Rechargeable batteries, also known as secondary battery systems, have wide applications in a range of electronic devices, possess the prominent advantage of achieving repeated conversion between electrical energy and chemical energy compared to primary batteries (Cheng *et al.*, 2011; Zhang *et al.*, 2015a; Aravindan *et al.*, 2014). Rechargeable batteries that existed in the market are Li-ion batteries, Li-air batteries, sodium-ion batteries, lead-acid (LA) batteries, nickel-metal hydride (NiMH) batteries, redox flow batteries, etc. (Li *et al.*, 2014; Luo *et al.*, 2013; Wang *et al.*, 2013; Goodenough and Kim, 2010). Although all types of batteries have their advantages, the inception of the Li-ion battery which comes with the highest workable energy density has changed the whole concept of possible application driven by the secondary battery system. The dominance of the Li-ion battery system over other secondary battery systems has largely been attributed to their high specific energy and power ratings as shown in Fig. 1.

Rechargeable Li-Ion Batteries

In the 1970s, a number of studies in the area of intercalation-based reactions have been made by various research groups (Reddy *et al.*, 2020). A pioneer work by Goodenough *et al.* (1979), which was later patented in 1979, proposed Li-based cathode material (LiCoO_2) and opened up a new window for the development of solid-solution-based materials. Further advances were later made by Armand *et al.* (Callens *et al.*, 1991; Suo *et al.*, 2013; Bouchet *et al.*, 2013; Zhou *et al.*, 2019). However, Sony manufactured the first commercial lithium-ion battery in the early 1990s. After countless researches on electrode materials, it has been realized that safety issues, economically sustainable processes, and performance optimization are the key factors that researchers and manufactures should focus on. A Li-ion battery system is usually referred to as a secondary battery in which energy is stored chemically through redox reactions. It generates a voltage of more than 3.5 V by combining cathode material and carbonaceous anode material, in which the lithium-ion inversely inserts and extracts. It has received intensive research and development focus because of its high energy density, long life cycle, and superior environmental friendliness (Xu *et al.*, 2012; Islam *et al.*, 2011; Goodenough and Kim, 2010; Chen *et al.*, 2018).

General Characteristics of Li-Ion Batteries

The lithium-ion battery (LIB) mainly consists of four primary components: the anode, cathode, separator, and electrolyte, for which a variety of materials can be used. The cathode acts as a positive electrode that accepts the electrons, while the anode acts as a negative electrode that donates the electrons during the discharge cycles. The electrodes do not touch each other but are electrically connected by the electrolyte. The separator, usually a polymer-based porous membrane, prevents the mixing between the electrodes, however, allows ions to flow. Fig. 2 illustrates schematically the working principles of LIBs. During charging, Li^+ ions move from cathode to anode through the electrolyte and return during discharging. This kind of electron flow through the external circuit provides electrical power (Chen *et al.*, 2018). The performance of the lithium-ion battery greatly depends on the structure and the properties of the materials used, thus the performance has been gradually improved with the development of new materials as well as various procedures. It has wide applications as an energy storage system in portable and smart electrical devices (e.g., cell phones, MP3 devices, cameras, and laptops), electric vehicles, and smart electrical grids (Besenhard and Winter, 2002). Nowadays, the LIB market is moving from small-scale applications to large-scale applications where more electric power is required such as Electric Vehicles (EVs) and Energy Storage Systems (ESSs) (Kim *et al.*, 2012).

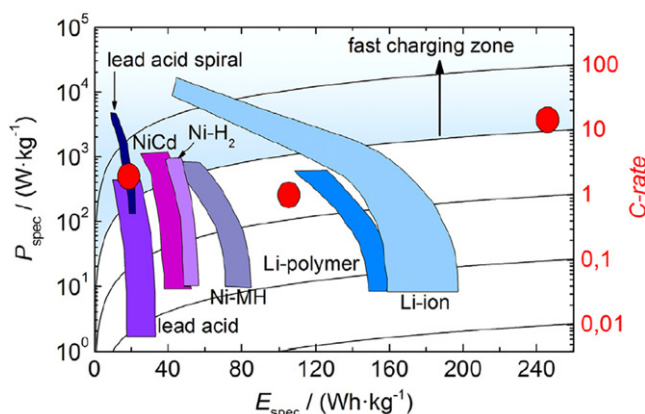


Fig. 1 A Ragone plot depicting the range of energy density and power density of commonly used battery systems. Reproduced for Pelz, A., Grünebaum, M., Wiemhöfer, H.-D., 2018. Hybrid electrolytes for lithium ion and post lithium ion batteries. In: Wandelt, K. (Ed.) Encyclopedia of Interfacial Chemistry. Oxford: Elsevier, pp. 660–673. <https://doi.org/10.1016/B978-0-12-409547-2.14190-3>.

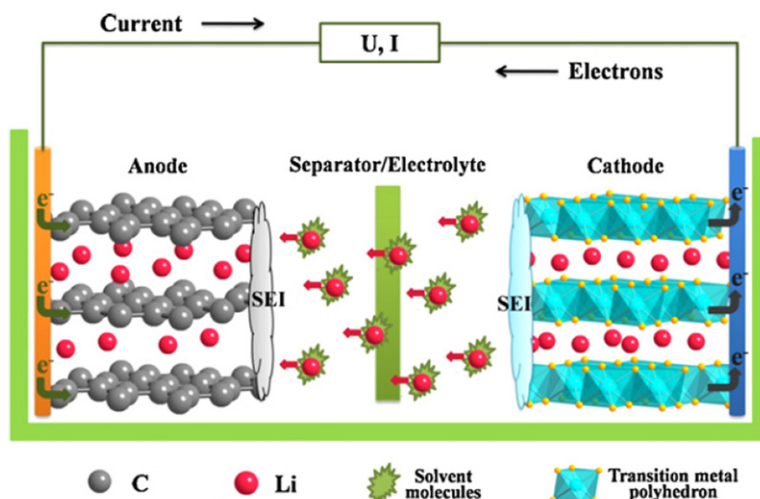


Fig. 2 Schematic illustration of working principles of lithium-ion battery (charging). Reproduced from Xu, B., *et al.*, 2012. Recent progress in cathode materials research for advanced lithium ion batteries. *Materials Science and Engineering R: Reports* 73 (5–6), 51–65. doi:10.1016/j.mser.2012.05.003.

Limitations of Li-Ion Batteries

Li-ion battery (LIB) is recognized as a 'critical material' due to the fundamental properties of the electrode materials. In most cases, it operates between 1.5.5 and 4.2 V, where a lower voltage degrades the Copper (Cu) foil (anode current collector), while a higher one forms reactive Li dendrites increasing the potential safety hazards of the products (Tarascon and Armand, 2001). Statistics show that nearly about 30%–50% of the world population are not aware of the potential hazard of post-use products in portable batteries (Sonoc and Jeswiet, 2014). The metallic Li is highly reactive when it comes in contact with moisture. Besides, the presence of a flammable electrolyte inside the battery could cause an explosion and emit harmful gases (such as hydrogen fluoride, HF) in the event of mechanical damages, overheating, or degradation phenomena, and thus exposing people to severe injuries (Sonoc *et al.*, 2015). Besides, it also has been noticed that the available lithium-ion battery could not meet the increasing energy demands for high energy density in large-scale applications such as electric vehicles. The excess layered oxides of lithium are responsible for a huge capacity loss, which slows down the lithium-ion diffusion rate at the end of the first charging. It significantly limits lithium-ion batteries' practical applications. This problem results mainly from the low specific capacity of the cathode materials (Islam *et al.*, 2011; Karkoschka *et al.*, 2006; Amine *et al.*, 2014; Wang *et al.*, 2016; Wu *et al.*, 2015; Zhong *et al.*, 2016). Efforts and steps have been made to overcome the limitations mentioned above to improve the battery performance. Enhancing the capacity of cathode materials is also imperative to achieve superior performance of the LIBs. The electronic conductivity or lithium-ion mobility of LIBs can be improved by following three techniques: (1) applying conductive carbon coating (Dominko *et al.*, 2005), (2) particle size reduction (Delacourt *et al.*, 2006), and (3) supervalent or isovalent cation doping (Chen *et al.*, 2009).

Cathode Material

The cathode material plays the most crucial role in determining the Li-ion batteries' performances, such as energy density, capability, thermal stability, and effective potential window. It also contributes and catalyzes the electrochemical reactions directly or indirectly (Cheng and Chen, 2012; Yi *et al.*, 2015; Islam and Fisher, 2014).

Types of Cathode Materials

Based on the crystal structure, various cathode materials are intensively investigated and classified such as layered mixed oxides (LiCoO_2 , LiNiO_2 , $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$, $\text{LiNi}_{0.05}\text{Mn}_{0.5}\text{O}_2$, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and $\text{Li}_{1.2}\text{Cr}_{0.4}\text{Mn}_{0.4}\text{O}_2$), Zigzag (LiMnO_2), Mn-based spinels (LiMn_2O_4 , LiCoMnO_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and LiCoVO_4), and polyanion type (LiFePO_4 , LiMnPO_4 , $\text{Li}_2\text{FeSiO}_4$, $\text{Li}_2\text{MnSiO}_4$, $\text{Li}_2\text{NiSiO}_4$, and $\text{Li}_2\text{CoSiO}_4$). These are the major types of cathode materials for lithium-ion batteries. Some other proposed cathode materials (e.g., organic, sulfur, air, and conversion cathodes) are still under investigation (Gong and Yang, 2011).

Polyanion type cathode materials

Of all, polyanion-type cathode materials have drawn attention due to their advantageous material properties such as high capacity, high redox potential, low cost, battery safety, and good thermal stability for electric devices (Chen and Richardson, 2010). Various polyanion compounds (such as borates (LiMBO_3), phosphates (LiMPO_4), pyrophosphates ($\text{Li}_2\text{MP}_2\text{O}_7$), and silicates ($\text{Li}_2\text{MnSiO}_4$)) have been

investigated as cathode material for lithium-ion batteries due to their impressive properties. Compared to conventional layered oxides and spinel cathode materials, the theoretical capacity of polyanion cathodes is very high ($170\text{--}330\text{ mAh g}^{-1}$). The borates with the lightest polyanion unit (BO_3) have a theoretical capacity of $\sim 200\text{ mAh g}^{-1}$, and the phosphates have a theoretical capacity of $\sim 170\text{ mAh g}^{-1}$. The pyrophosphates and the silicates exhibit theoretical capacity ~ 220 and 330 mAh g^{-1} , respectively. The enhanced theoretical capacity of pyrophosphates and silicates can be attributed to the possibility of two lithium-ion insertion/extraction per transition metal in the electrode material (Vajeeston and Fjellvåg, 2017). Recently, silicate cathodes, especially $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$, have attracted significant interest (Nytén *et al.*, 2005; Sirisopanaporn *et al.*, 2011).

The cathode materials based on orthosilicates such as Li_2MSiO_4 (where $\text{M} = \text{Fe, Mn, Co, Ni, etc.}$) are a new class of polyanion cathodes comprised of tetragonally packed oxide ions (a distorted form of hexagonal close packing) in which half of the tetrahedral sites are occupied by cations (Eames *et al.*, 2012). Due to the change of cation site ordering and distortion of the tetrahedra, various complex polymorphisms of Li_2MSiO_4 exist. It has been reported that the Li_2MSiO_4 shows three common polymorphs: (1) monoclinic $\text{P2}_1/\text{n}$, (2) orthorhombic $\text{Pmn}2_1$, and (3) orthorhombic Pmnb . Fig. 3 resembles the crystal structure of $\text{Li}_2\text{FeSiO}_4$ which has been observed alongside the b -axis. There are three polymorphs commonly observed for $\text{Li}_2\text{FeSiO}_4$ – monoclinic $\text{P2}_1/\text{n}$, orthorhombic Pmnb , and orthorhombic $\text{Pmn}2_1$. The linking mechanisms of various tetrahedra (LiO_4 , SiO_4 , and FeO_4) are different in these above polymorphs (See Fig. 4). The Li site in orthorhombic $\text{Pmn}2_1$ and Li(2) site in monoclinic $\text{P2}_1/\text{n}$ polymorph are surrounded by four Fe^{2+} ions. On the other hand, the Li site in orthorhombic Pmnb and Li(1) site in monoclinic $\text{P2}_1/\text{n}$ polymorph are surrounded by three Fe^{2+} ions (Ni *et al.*, 2017; Chen *et al.*, 2013). In other words, both the lithium sites are present in monoclinic $\text{P2}_1/\text{n}$ polymorph. These three polymorphs of $\text{Li}_2\text{FeSiO}_4$ evolve with varying heat treatment temperatures. At lower temperature ($\sim 200^\circ\text{C}$) orthorhombic $\text{Pmn}2_1$ is stable, but at higher temperature ($\sim 700^\circ\text{C}$) it transforms to monoclinic $\text{P2}_1/\text{n}$ polymorph. The inversion temperature of another orthorhombic Pmnb is found to be $\sim 900^\circ\text{C}$ (Sirisopanaporn *et al.*, 2011; Eames *et al.*, 2012; Ni *et al.*, 2017). The redox potential varies with the changing polymorphs, though the factors behind the voltage difference are not fully understood.

The primary components of $\text{Li}_2\text{FeSiO}_4$ are iron and silicon. These two elements are among the most abundant elements on Earth and cheap as well. Furthermore, another outstanding advantage is that it is possible to extract more than one lithium ion per transition metal, resulting in a high theoretical capacity of about 333 mAh g^{-1} (Zaghib *et al.*, 2006; Chung *et al.*, 2002). Though, the theoretical capacity is calculated to be 166 mAh g^{-1} based on a reversible exchange of one Li-ion per formula unit. Moreover, $\text{Li}_2\text{MnSiO}_4$ (Dominko *et al.*, 2007; Deng *et al.*, 2010; Gummow *et al.*, 2012), $\text{Li}_2\text{CoSiO}_4$ (Gong *et al.*, 2007; Qing Wu *et al.*, 2009; Wu *et al.*, 2007), $\text{Li}_2\text{FeSiO}_4$ (Nytén *et al.*, 2005; Jun Guo *et al.*, 2009; Liu, 2009; Dahbi *et al.*, 2012; Dominko *et al.*, 2006; Hao *et al.*, 2012; Kalaiselvi and Manthiram, 2010; Kam *et al.*, 2011; Larsson *et al.*, 2006; Liivat and Thomas, 2010; Zhang *et al.*, 2010b), and LiFeSO_4F (Liu *et al.*, 2011) along with silicates have been examined for their interesting electrochemical potential as a cathode material.

Doping and its Effect on Cathode Materials

Doping methods alone cannot enhance the performance of cathode materials without a proper selection of doping material which plays a major role to achieve better performance. Based on the special attributes of doping elements, the electrochemical performance and structural stability of cathode materials can be adjusted. The functions of doping can be summarized as follows: (1)

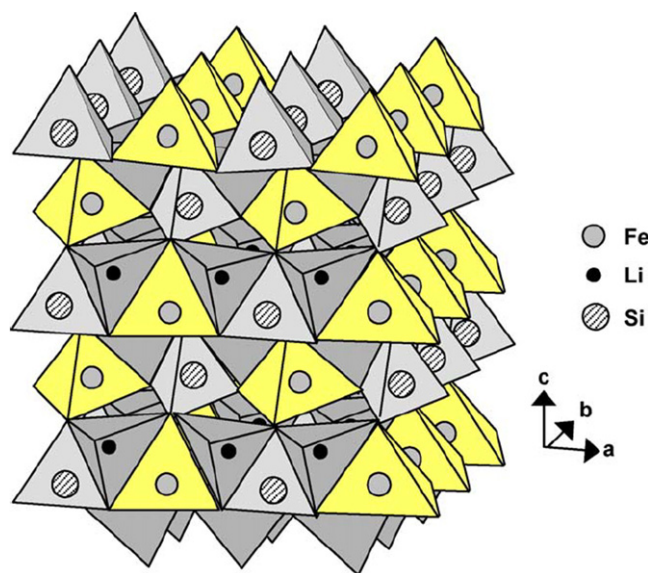


Fig. 3 The crystal structure of $\text{Li}_2\text{FeSiO}_4$ is viewed along the b -axis. All the cations are tetrahedrally coordinated with oxygen atoms. Reproduced from Zaghib, K., *et al.*, 2006. Structural, magnetic and electrochemical properties of lithium iron orthosilicate. *Journal of Power Sources*, 160 (2 SPEC. ISS.), 1381–1386. doi:10.1016/j.jpowsour.2006.03.023.

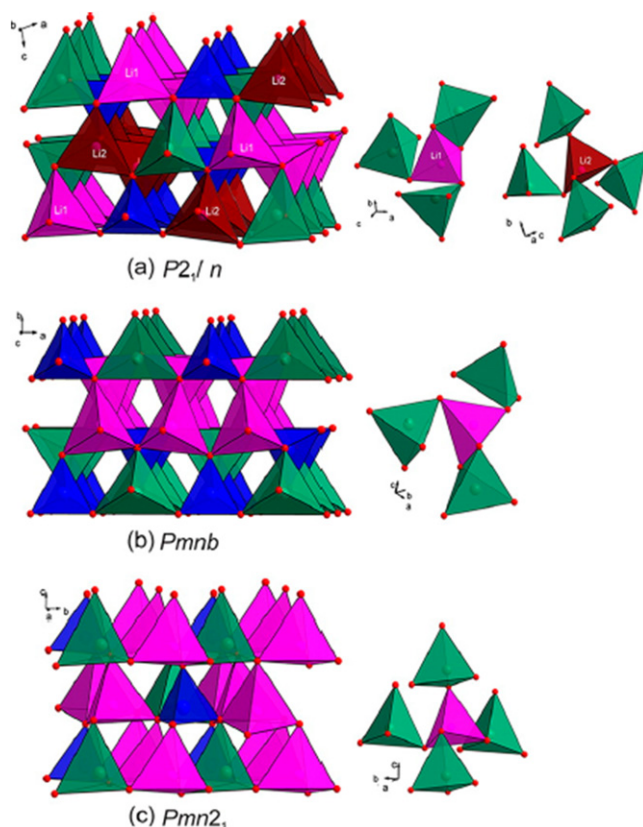


Fig. 4 Crystal Structures of $\text{Li}_2\text{FeSiO}_4$ polymorphs: (a) $P2_1/n$ space group, (b) $Pmnb$ space group, (c) $Pmn2_1$ space group. LiO_4 tetrahedra (pink and brown color); FeO_4 tetrahedra (green color); SiO_4 tetrahedra (blue color). This graphical representation shows the linkage mechanism of LiO_4 tetrahedra with the surrounding FeO_4 tetrahedra. Reproduced from Chen, R., Heinzmann, R., Mangold, S., *et al.*, 2013. Structural evolution of $\text{Li}_2\text{Fe}_{1-y}\text{Mn}_y\text{SiO}_4$ ($y = 0, 0.2, 0.5, 1$) cathode materials for li-ion batteries upon electrochemical cycling. The Journal of Physical Chemistry C 117 (2), 884–893. doi:10.1021/jp310935j.

forming an aliovalent substitution and multivalent substitution, owning electrochemically inactive property and increasing the electronic and ionic conductivity; (2) maintaining a stable structure; (3) suppressing oxygen release by strengthening transition metal (TM) oxide bond, and impacting the phase transformation during cycling. The doping elements often form a concentration-gradient distribution, enriched on the surface and decreased at the core, and facilitate structural stability. The selection of the synthesis process and doping elements together have a significant effect on the performance of cathode materials. Therefore, we have to be more careful while choosing the methods and doping elements. Improvement of the cathode materials' energy density is one of the most critical issues in the field of lithium-ion batteries. The possible strategies mainly include using cathode materials with a high voltage or with a reversible exchange of more than one lithium ion per unit formula, such as $\text{Li}_2\text{FeSiO}_4$ (LFS). Still, there are many challenges such as large irreversible capacity in the first circle, a voltage and capacity fading, sluggish lithium ion diffusivity associated with LFS materials that need to be resolved. Efforts have been made to improve the electrochemical performance of LFS. To date, various synthesis methods like reducing the particles size (Cui *et al.*, 2014; Fu *et al.*, 2013), coating the particles with carbon (Nytén *et al.*, 2005; Gong *et al.*, 2008; Zuo *et al.*, 2012; Hao *et al.*, 2012), doping/ substitution with a metal cation, including Mg^{2+} , Mn^{2+} , Cr^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} (Zhang *et al.*, 2010b; Chen *et al.*, 2013; Deng *et al.*, 2011; Guo *et al.*, 2010; Zhang *et al.*, 2014; Li *et al.*, 2011) have been developed and introduced to measure the structures and morphologies of the orthosilicates. Following the above-mentioned methods, various doping elements such as Mg, Co, Cr, Al, V, and N have been tried to improve the lithium metal silicate's electrochemical performance (Gao, 2014; Zhang *et al.*, 2015b; Deng *et al.*, 2014; Zhu *et al.*, 2015). The metal cation doping can effectively improve the intrinsic conductivity of cathode materials, such as LiFePO_4 , (Yuan *et al.*, 2011; Chung and Chiang, 2003) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, (Zhang *et al.*, 2012; Dong *et al.*, 2011) and $\text{Li}_2\text{FeSiO}_4$ (Zhang *et al.*, 2010b; Guo *et al.*, 2010; Deng *et al.*, 2011; Chen *et al.*, 2013). Supervalent or isovalent cation doping is also employed to improve the electrochemical performance of polyanion compounds (Chung *et al.*, 2002; Omenya *et al.*, 2011).

Effect of Doping on Lithium-Iron Silicate Materials

The development of novel lithium-ion battery cathode materials with high specific capacity has been a major challenge in the scientific arena for the last two decades. The conventional cathode materials, like olivine-type (Hsu *et al.*, 2004), $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

Table 1 The effect of various dopants on $\text{Li}_2\text{FeSiO}_4$ -based Li-ion battery system

Dopant	Synthesis method	Discharge capacity	Capacity retention ratio	References
V	Solid-state reaction assisted with refluxing process	220 mAh g^{-1}	78.7 after 50 cycles	(Zhang <i>et al.</i> , 2015c)
Mg	Sol-gel method	153 mAh g^{-1}	98.6% after 50 cycles	(Zhang <i>et al.</i> , 2010a)
Cd	Solid-state reaction assisted with refluxing process	191 mAh g^{-1}	96.9% after 40 cycles	(Zhang <i>et al.</i> , 2014)
Ni	Combination of wet-process method and solid-state reaction	160 mAh g^{-1}	96.1% after 10 cycles	(Ming Li <i>et al.</i> , 2009)
Co	Solid-state reaction assisted with refluxing process	199 mAh g^{-1}	81.7% after 50 cycles	(Zhang <i>et al.</i> , 2015b)
Zn	Sol-gel method	133 mAh g^{-1}	94.8% after 30 cycles	(Deng <i>et al.</i> , 2011)
Cr	Sol-gel method	160 mAh g^{-1}	90.1% After 20 cycles	(Zhang <i>et al.</i> , 2010b)
Mn	Mechanical activation-solid-state reaction	158 mAh g^{-1}	94.3% after 30 cycles	(Guo <i>et al.</i> , 2010)

(Chen *et al.*, 2019), silicate-based oxides (Zhu *et al.*, 2019), and manganese-based layered lithium-rich cathode (LLRC) material have received attention due to their higher specific capacity (Zhu *et al.*, 2019). However, these electrode materials generally have a low lithium-ion migration rate, a large irreversible capacity in the first circle, severe voltage and capacity fading, and oxygen release issues, which hinders its practical applicability (Yu *et al.*, 2018). Therefore, it is necessary to find out alternative materials to overcome these inherent defects. In this article, the doping effect of V, Mg, Cd, Ni, Co, Zn, Cr, Mn into $\text{Li}_2\text{FeSiO}_4$ (LFS) is discussed elaborately. The discussion is mainly focused on revealing the origin of the doping effect, which provides some useful information for modifying and designing relevant LFS materials in the future. The doping of LFS materials by various metallic cations is described in Table 1 to understand the effects.

V-doping

Vanadium is a promising candidate for partial substitution of the transition metal or silicon in Li_2MSiO_4 (where $\text{M} = \text{Fe, Mn, Co}$) compounds. Vanadium oxides offer the advantages of being cheap, easy to synthesize, abundant on Earth, possess high energy density, and thus has attracted much interest (Wang *et al.*, 2006; Tang *et al.*, 2013; Pang *et al.*, 2013; Zhou *et al.*, 2012; Wu *et al.*, 2013; Pan *et al.*, 2012; Zhao *et al.*, 2013; Bao *et al.*, 2013). Recently, ammonium vanadium oxide nanostructures have received a great deal of attention as lithium-ion battery cathode material. Besides, vanadium doping, alone, has been proven to be very effective. The substitution of vanadium can enhance the capacity of $\text{Li}_2\text{FeSiO}_4$ since several oxidized vanadium states up to V^{5+} are available (Gao, 2014).

A density functional theory calculation conducted by Li *et al.* (2011) showed that vanadium substitution for iron in $\text{Li}_2\text{FeSiO}_4$ is thermodynamically stable up to 50 mol% and higher capacity can be obtained by reversible exchange of more than one lithium-ion (Li *et al.*, 2011). 5 and 10 mol% V-doped $\text{Li}_2\text{MnSiO}_4$ (LMS) showed effectiveness in reducing the grain size, enhancing the electrochemical properties, purifying the crystalline phase, and improved diffusion coefficients (Hwang *et al.*, 2016). Hao *et al.* (2012) investigated the effects of vanadium substitution at different sites (Fe/Si) and found that $\text{Li}_2\text{FeSi}_{0.9}\text{V}_{0.1}\text{O}_4/\text{C}$ exhibits better electrochemical performance than $\text{Li}_2\text{Fe}_{0.9}\text{V}_{0.1}\text{SiO}_4/\text{C}$ (Hao *et al.*, 2012). Irrespective of V-incorporation on either Fe or Si sites, higher capacity can be achieved where more than one Li-ion is exchanged.

Mg-doping

Magnesium is the tenth most abundant element in the Earth's crust and has been utilized as a dopant for cathode material in lithium-ion batteries. It has been observed that Mg-doping improves the discharge capacity and cycle stability of $\text{Li}_2\text{FeSiO}_4$. In addition to the above-mentioned advantages, Mg-doping increases the Li-ion diffusion coefficient and decreases the charge transfer resistance of $\text{Li}_2\text{FeSiO}_4$ cathode. Both pristine and doped cathode materials have a monoclinic structure (space group: $\text{P}2_1/\text{n}$), and their lattice parameters are similar. Electrochemical impedance analysis shows a decrement in the magnitude of the charge-transfer resistance of $\text{Li}_2\text{FeSiO}_4$ due to Mg-doping. Moreover, it increases the Li-ion diffusion coefficient by an order of magnitude. It also exhibits higher reversible capacity at high rates. Up to 5 mol% Mg^{2+} doping retains the paramagnetic monoclinic structure and lattice parameter. But, when the doping exceeds 10 mol% fractions, a magnetic phase segregates within the sample. Particle agglomeration forms small sphere-like particles with a broad particle size distribution (Jaén *et al.*, 2015a). Furthermore, Mg^{2+} ion is unchangeable during cycling which stabilizes the crystal structure, and thus enhances the cycle stability of $\text{Li}_2\text{FeSiO}_4$ (Liu *et al.*, 2006). In several studies, it has been found that Mg-doping strengthens structural stability during the lithiation-delithiation (Chen *et al.*, 2018; Besenhard and Winter, 2002; Kim *et al.*, 2012; Gao *et al.*, 2018; Georgi-Maschler *et al.*, 2012). Zhang *et al.* (2010a,b) in their study partially substituted iron with magnesium (up to 3%, mole fraction) and reported that the doping improves the electrochemical properties of the $\text{Li}_2\text{FeSiO}_4$ cathode materials (Zhang *et al.*, 2010a). The resulting compound, $\text{Li}_2\text{Fe}_{0.97}\text{Mg}_{0.03}\text{SiO}_4$, also exhibits better cyclic stability and reversibility. The improved electrochemical performance can be attributed to its enhanced lithium-ion diffusion capability, reduced electrochemical impedance, and enhanced structural stability.

Cd-doping

Cd-modified $\text{Li}_2\text{FeSiO}_4$ (Cd-LFS) composites were successfully synthesized and reported. Cd-doping does not change the monoclinic structure and the valence state of Fe in LFS. It can increase the defect concentration and the electronic conductivity of LFS by increasing the Li-ion diffusion process. Zhang *et al.* (2014) successfully synthesized cadmium incorporated LFS/C

composites (6Cd-LFS/C) by solid-state reaction assisted refluxing (Zhang *et al.*, 2014). The electrochemical measurement of the composite exhibited an initial discharge specific capacity of 191.3 mAh g^{-1} with an excellent coulombic efficiency of 96.9%. However, its average specific capacity after 200 cycles decreased to 112.4 mAh g^{-1} at 3 C, which is much higher than that of pristine form LFS/C (79.3 mAh g^{-1}). The improved electrochemical performance of Cd-modified LFS/C cathode material can be attributed to increased defect concentration, enhanced electronic conductivity, decreased charge transfer resistance, and enhanced Li-ion diffusion coefficient.

Ni-doping

The electrochemical performance of $\text{Li}_2\text{FeSiO}_4$ cathode is improved upon modification by Ni substitution (Ming Li *et al.*, 2009). However, Deng *et al.* (2011) found that Ni^{2+} doped $\text{Li}_2\text{FeSiO}_4$ exhibited more unsatisfactory electrochemical performance compared to the undoped orthosilicate (Deng *et al.*, 2011). In their comparison with the $\text{Li}_2\text{FeSiO}_4$ electrode materials, the Ni-doped samples show some extra reflections with a little increase in unit cell volume and the lattice parameters show a monotonic change. Up to 5 mol% of Ni^{2+} doping can retain the monoclinic structure, whereas samples doped with $\geq 10\%$ Ni^{2+} show the existence of FeNi and FeNi_3 . Therefore, it is advisable to keep the doping concentration at less than 10%. Although the Ni-doping favors the segregation of undesirable impurities, yet it does not destroy the lattice structure of $\text{Li}_2\text{FeSiO}_4$ (Jaén *et al.*, 2015b). An initial discharge capacity of 160.1 mAh g^{-1} of $\text{Li}_2\text{Fe}_{0.9}\text{Ni}_{0.1}\text{SiO}_4/\text{C}$ cathode was reported by Li *et al.* (2009). However, the discharge capacity was reduced to 153.9 mAh g^{-1} after 10 cycles which showed poor long-term cyclability.

Co-doping

Without changing the monoclinic structure of $\text{Li}_2\text{FeSiO}_4$ and the oxidation state of Fe, cobalt has been successfully doped into the lattice of $\text{Li}_2\text{FeSiO}_4$. It helps to enhance the electrochemical performance of $\text{Li}_2\text{FeSiO}_4$ because of the defect concentration and enhancement of electronic conductivity. The Co-doped samples also exhibit higher reversible capacity at any C-rate compared to the pristine sample (Zhang *et al.*, 2015b). The enhancement in the electrochemical performance is attributed to reduced particle size, increased defect concentration, improved electronic conductivity, decreased charge-transfer resistance, and the enhanced Li-ion diffusion coefficient. It indicates that this Co-doped $\text{Li}_2\text{FeSiO}_4$ is a promising alternative for next-generation lithium-ion batteries.

Zn-doping

Zn-doped samples demonstrated better cycling, electrochemical performance, and structural stability compared to the undoped ones. $\text{Li}_2\text{ZnSiO}_4$ can be crystallized in space group $\text{Pmn}2_1$ (orthorhombic, the same as $\text{Li}_2\text{FeSiO}_4$) (Jousseume *et al.*, 2003). Moreover, $\text{Li}_2\text{ZnSiO}_4$ is a Li-ion conductor with high ionic conductivity. Therefore, it is interesting to investigate the doping effect of Zn on the structural and electrochemical characteristics of $\text{Li}_2\text{FeSiO}_4$. Compared with the undoped $\text{Li}_2\text{FeSiO}_4$, the Zn-doped sample exhibits lower electrode polarization, higher discharge capacity, and better electrochemical reversibility. These improvements can be attributed to improving lithium diffusion capability. Zn-doping also increases the stability of electrode materials which acts as the main reason behind the better lithium-ion diffusivity. Zn^{2+} does not oxidize/ reduce during the charge/ discharge cycles and thus lessen the change of the crystal lattice. This stabilization effect can protect the diffusion path of lithium-ion from being distorted and improves the lithium diffusivity (Deng *et al.*, 2011).

Cr-doping

Zhang *et al.* (2010a,b) in a comparative study found that the Cr-doped samples have no extra reflections, which is an indication of Cr infiltration in $\text{Li}_2\text{FeSiO}_4$ structure without impure phase formation (Zhang *et al.*, 2010b). The Cr-doped samples also show faster activation, lower electrode polarization, higher reversible capacity, and better rate capability, which can be attributed to the large surface area and smaller particle size. It also increases the specific surface area of $\text{Li}_2\text{FeSiO}_4$ and induces defects in the crystal lattice, which lowers the electrode polarization and improves lithium-ion mobility. The highest capacity is found to be obtained at 3% Cr-doping (Zhang *et al.*, 2010b). Beyond 3% Cr-doping, the capacity decreases. This can be attributed to the decrease in the amount of Fe. As the Cr does not take part in the charge-discharge process, the capacity is decreased due to Fe substitution by Cr when the amount of Cr is $> 3\%$. The Cr-doped sample ($\text{Li}_2\text{Fe}_{0.97}\text{Cr}_{0.03}\text{SiO}_4$) was found to be more porous than the $\text{Li}_2\text{FeSiO}_4$ sample. This is a very important characteristic because porosity is the key reason behind the better performance of an electrode. For a highly porous material, the electrolyte can easily penetrate the pores to enlarge the area for electrode reaction. Therefore, better electrochemical performance can be expected for the $\text{Li}_2\text{Fe}_{0.97}\text{Cr}_{0.03}\text{SiO}_4$ sample compared to the $\text{Li}_2\text{FeSiO}_4$ (Zhang *et al.*, 2010b).

Mn-doping

$\text{Li}_2\text{MnSiO}_4$ cathode material has a higher theoretical capacity (based on $\text{Mn}^{2+}/\text{Mn}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couples) than $\text{Li}_2\text{FeSiO}_4$, but its cyclic stability decreases sharply because of its poor structural stability (Deng *et al.*, 2010; Guo *et al.*, 2010). Combining the advantages of $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$, Deng *et al.* (2009) proposed $\text{Li}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{SiO}_4$ ($x = 0.3, 0.5, 0.7$) as a cathode material which exhibited first discharge capacity (than $\text{Li}_2\text{FeSiO}_4$) and better cyclic stability (than $\text{Li}_2\text{MnSiO}_4$) (Deng *et al.*, 2009). The Mn substituted samples also have higher redox potentials than $\text{Li}_2\text{FeSiO}_4$. On the other hand, poor cycling performance and electrochemical reversibility are also induced with increasing content of Mn substitution. Therefore, to overcome the

challenges encountered, partial substitution of Fe with Mn (optimum content) in $\text{Li}_2\text{FeSiO}_4$ can be a promising cathode material for lithium-ion batteries.

Effect of Co-Doping on Lithium-Iron Silicate Materials

The thermal stability of $\text{Li}_2\text{FeSiO}_4$ made it an excellent cathode material for next-generation battery applications. Doping is a proven technique for improving the electrochemical performances of $\text{Li}_2\text{FeSiO}_4$ (discussed in previous sections). For further enhancement of electrochemical performances of $\text{Li}_2\text{FeSiO}_4$ cathode material, an introduction of a second dopant has been widely explored recently. Mn^{2+} is found to be one of the co-dopant in most cases to exploit the possibility of extracting more than one Li-ion per formula unit by using an appropriate Fe/Mn ratio with the general formula $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{SiO}_4$. As a second dopant, the cations of V, Ti, Al, Mg, Zn, and Ni are mostly studied.

Zhang *et al.* (2019) studied Mn and V Co-doped $\text{Li}_2\text{Fe}_{0.8(1-x)}\text{Mn}_{0.2(1-x)}\text{V}_x\text{SiO}_4$ ($x = 0, 1\%, 2\%$, and 5%) prepared via citrate-assisted sol-gel process (Zhang *et al.*, 2019). The best initial discharge specific capacity of 134.5 mAh/g at 0.1 C rate was reported when $x = 1\%$ and 80% of the capacity was retained after 100 cycles. On the other hand, the initial discharge capacity of single-doped $\text{Li}_2\text{Fe}_{0.8}\text{Mn}_{0.2}\text{SiO}_4$ was found not only lower but the capacity retention also decreased to 76% . The improved capacity of the V co-doped sample can be attributed to the enhanced Li-ion diffusion coefficient achieved by V-doping. In an earlier work by Toyama and Takahashi (2015), V-substituted (as a second dopant) $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$ cathode material was prepared using solid-state reaction where V^{5+} is substituted for Si^{4+} in $\text{Li}_{2+x}\text{Fe}_{0.5-x/2}\text{Mn}_{0.5-x/2}\text{Si}_{1-x}\text{V}_x\text{O}_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) by maintaining electroneutrality (Toyama and Takahashi, 2015). However, no strong evidence was found to determine the substitution site of V. The maximum first cycle discharge capacity was obtained as 197 Ah/kg when $x = 0.2$, while $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$ exhibited 134 Ah/kg . For $x > 0.2$, the capacity deteriorates which attributes to the decreased content of transition metal ratio in $\text{Li}_{2+x}\text{Fe}_{0.5-x/2}\text{Mn}_{0.5-x/2}\text{Si}_{1-x}\text{V}_x\text{O}_4$.

Liu *et al.* (2019) described the effects of co-doping of Mn^{2+} and Ti^{4+} at Fe-site in $\text{Li}_2\text{FeSiO}_4$. The composite $\text{Li}_2\text{Fe}_{1-x-y}\text{Mn}_x\text{Ti}_y\text{SiO}_4/\text{C}$ ($x = 0.05\text{--}0.20$, $y = 0.02\text{--}0.08$) was prepared by combining the sol-gel, spray drying, and microwave synthesis process (Liu *et al.*, 2019). The results indicate that the modified composite has a higher specific capacity, better cyclic stability, and faster lithium-ion diffusion rate as well as lower impedance and better reversibility when x and y are 0.15 and 0.04 , respectively.

A study conducted by Li *et al.* (2016a,b), showed the synthesis of Mn and Al co-doped $\text{Li}_2\text{Fe}_{0.8-x}\text{Mn}_{0.2}\text{Al}_x\text{SiO}_4$ ($x = 0.05$ and 0.1) by a solid-state reaction route (Li *et al.*, 2016b). In comparison with the single-doped samples, the co-doped samples showed no significant difference in the morphology and particle size after the modification. Interestingly, the co-doping did not affect positively on discharge capacity, however, a better cycling performance was reported. The decreased capacity is attributed to the increased impurity and Al^{3+} inertia. The reported best initial discharge capacity was found to be 159.3 mAh/g when $x = 0.05$ ($\text{Li}_2\text{Fe}_{0.75}\text{Mn}_{0.2}\text{Al}_{0.05}\text{SiO}_4$), and 78% of the capacity was retained after 50 charge/discharge cycles. The improved cycling stability may be attributed to the Al^{3+} co-dopant which is believed to increase the structural stability during cycling and improved Li-ion diffusion.

Li *et al.* (2016a,b) investigated the effect of Mn^{2+} and $\text{Mg}^{2+}/\text{Zn}^{2+}$ co-doped $\text{Li}_2\text{Fe}_{0.8-x}\text{Mn}_{0.2}\text{M}_x\text{SiO}_4$ ($\text{M} = \text{Mg}$ and Zn , $x = 0.05$ and 0.1) prepared by solid-state reaction (Li *et al.*, 2016a). The objective was to incorporate electrochemically inactive M^{2+} ions which can strengthen the crystal structure, and thus improve the cycling performance. In comparison with the single-doped (Mn^{2+}) electrodes, the co-doped samples (Mn^{2+} and Mg^{2+}) showed higher cycling performance which leads to higher capacity retention after 50 cycles. However, incorporation of Zn^{2+} as Mn/Zn co-doping, the samples exhibited decreased electrochemical performance due to the increased internal polarization, hindered charge transfer, decreased Li^+ diffusivity. The results of the study suggested that the Mg^{2+} along with Mn^{2+} improve the structural stability which ultimately shows better electrochemical performance compare to single doped (Mn^{2+} at Fe-site) $\text{Li}_2\text{FeSiO}_4$.

Recently, in a similar study using the base cathode as $\text{Li}_2\text{Fe}_{0.8}\text{Mn}_{0.2}\text{SiO}_4$ (Mn-doped), Li and Gao (2021) explored Ni as a second-dopant in $\text{Li}_2\text{Fe}_{0.8-x}\text{Mn}_{0.2}\text{Ni}_x\text{SiO}_4$ ($x = 0.05$ and 0.1) (Li and Gao, 2021). Promising electrochemical performance of the co-doped sample was reported. The initial discharge capacities reached 164 mAh g^{-1} when $x = 0.1$ ($\text{Li}_2\text{Fe}_{0.7}\text{Mn}_{0.2}\text{Ni}_{0.1}\text{SiO}_4$). The incorporation of Ni as a second dopant is believed to reduce the electronic band gap, and thus promote Li^+ insertion/de-insertion behavior in the co-doped material.

Conclusions

This article discusses the effects of doping on lithium-iron silicate cathode material in lithium-ion batteries. This $\text{Li}_2\text{FeSiO}_4$ has drawn attention due to its advantageous material properties such as low toxicity, environmental friendliness, low cost, high discharge power, high thermal stability through strong Si–O bonding, which theoretically allow a two-electron exchange per formula unit and long service life. However, a large irreversible capacity in the first circle, a voltage and capacity fading, sluggish lithium ion diffusivity limits its practical applicability. Efforts and steps have been made to overcome such limitations through cation-doping, carbon-coating, and particle downsizing. Among the mentioned techniques, cation-doping, especially with Mg^{2+} , Mn^{2+} , Cr^{2+} , Ni^{2+} , Cu^{2+} , etc., has drawn much attention among researchers. $5\text{--}10 \text{ mol}\%$ V-doping showed effectiveness in enhancing the electrochemical properties and improved diffusion coefficients, although achieving phase purity of the doped cathode remains a major challenge. Co-doping, Mn (first-dopant) along with the second-dopant as V, Ti, Al, Mg, and Ni, was found to be effective to enhance the electrochemical properties of $\text{Li}_2\text{FeSiO}_4$ -based cathode materials.

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ZnO Varistors – The Ideal Microstructure and Characteristics, and Methods Investigated and Developed to Achieve These

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Abstract

ZnO-Bi₂O₃-Sb₂O₃ varistors have been extensively studied since their discovery 5 decades ago. Their function in protecting increasingly sensitive electronic components by absorbing random surges of energy is even more important today. Also, the metal oxides from which they are made from are becoming even more precious. Their electrical characteristics are highly dependent on their microstructural characteristics which are highly dependent on their composition and methods used. The purpose of this article is to explain the ideal microstructure required to obtain the ideal electrical characteristics, the powder preparation methods investigated and developed to achieve it, and some future directions are outlined.

Key Points

- The ideal electrical properties include a low leakage current, a high voltage per unit length (V mm^{-1}), a high nonlinear coefficient, a high upturn current and energy capability, and after high current pulses a minimum shift in the low current characteristics.
- The microstructure of ZnO-Bi₂O₃-Sb₂O₃ varistors is complex. It contains several phases, types of grain boundaries and pores, all of which have different electrical characteristics.
- An ideal microstructure should have a narrow distribution in ZnO grain size, be homogeneous, and contain no pores.
- The composition and processing methods have a significant effect on the final microstructure.
- A significant amount of work has been investigated on the powder preparation stage in particular the chemical methods with the purpose to obtain maximum homogeneity and specific surface area. Mechanical methods have received increasing attention with the development of new milling methods and harder materials.
- The mechanical and chemical methods investigated to make ZnO-Bi₂O₃-Sb₂O₃ based powders have a large effect on the microstructural and electrical characteristics.
- Topics concerning powder preparation for future research is outline.
- Explain the background including the applications, electrical characteristics, microstructure, and the relationship between the microstructure and electrical characteristics.
- Explain the effect of microstructural disorder and consequently the characteristics that an ideal microstructure for ZnO-Bi₂O₃-Sb₂O₃ varistors should have.
- Explain the powder methods investigated and developed, mechanical and chemical, to achieve ideal microstructures and thus electrical properties.
- Draw conclusions from the methods investigated and developed to achieve the ideal microstructure, and
- Outline some topics for future research.

Introduction

Definition

Zinc oxide varistors are complex, multiphase, polycrystalline, doped, metal oxide, solid state, semiconducting ceramics. Their electrical resistance is a non-linear (non-Ohmic) function of applied voltage, which was reported by [Matsuoka \(1971\)](#) fifty years ago. Their very steep non-linear current-voltage (I-V) curve allow them to support widely varying currents over a narrow voltage range ([Matsuoka, 1981](#); [Gupta, 1990](#); [Clarke, 1999](#)). They are made of ZnO plus other metal oxide additives such as bismuth, antimony, cobalt, manganese, and nickel, and their unique non-linear electrical properties arise from internal interfaces between the ZnO grains in the ceramic microstructure. They are also known as non-linear resistors, voltage dependent resistors and over voltage suppressors. The varistor derives its name from the fact that it acts as a variable resistor whose resistance depends mainly on the applied voltage. The higher the voltage the lower is the resistance. It is this characteristic that makes surge protection using varistors possible.

Justification

Although ZnO varistors have been available commercially for about 45 years in various shapes and sizes ranging from multi-layered devices to surface mount, tubular, axial, radial and arrestors, there is a continuous trend towards miniaturization, higher performance per unit volume, cost reduction, longer life, higher reliability, and higher yields in production. In the semiconductor industry there is a drive towards replacing numerous components by a single device, hence driving up the magnitude of sensitivity and consequently the unreliability of these devices to over voltage surges. Not only are manufacturers increasingly using over voltage suppressors, but they are looking for overvoltage suppressors with increasingly higher performance in terms of voltage suppression, energy absorption and reliability.

Many of the elements, including cobalt and nickel, used in ZnO varistors are in high demand, such as in solving the climate crisis with ever more efficient batteries for cars and mobile phones, and the mines from which they are sourced are few in numbers and have limited capacity. In addition, the implications of the accelerated rate at which these elements have been extracted recently from these mines may be of concern towards the health of the local human population, culture, ecology, and the environment (Watts, 2019). Several precious metals, including silver, platinum, and palladium, are used for the electrodes in ZnO varistors. According to a recent United Nations report over 10 billion dollars of precious metals are dumped annually and only 17% of which is recycled (Carrington, 2020). Less raw materials are needed if electronic products, including ZnO varistors, are designed with higher capability, reliability, longer lives and higher production yields. The continued requirement for downsizing in electronic components combined with improved performance demands greater understanding between the microstructural parameters required to influence the I-V characteristics of zinc oxide varistors.

Aim

The aim of this article is to explain the ideal microstructure required to obtain ZnO-Bi₂O₃-Sb₂O₃ varistors with ideal electrical characteristics, the powder methods, mechanical and chemical, developed to date to achieve it, and some areas for future work.

Background/Fundamentals

Applications

Because of their unique non-linear I-V electrical characteristic ZnO varistors can absorb, or pass to ground, large amounts of energy and are thus used as transient surge suppressors or voltage regulators. The delivery of current energy in any electrical system is not constant. Surges of voltages greater than the norm can occur both predictably and unpredictably. Voltage transients are defined as short duration surges of electrical energy and are caused by the sudden release of energy that was previously stored such as electrostatic discharge (E.S.D.), or induced by other means, such as heavy inductive loads, random surges (peaks, transients, or spikes) of voltage in power lines caused by switching and lightning strikes (Littelfuse, 2017). Electronic components are sensitive to stray electrical transients. These surges can cause damage, malfunction, or destroy electronic components. Varistors are used to protect electronic components within circuits. The near symmetrical I-V curve, sharp breakdown characteristics shown in Fig. 1 and Fig. 2 enable the varistor to provide excellent transient suppression performance. When exposed to high voltage transients the varistor impedance (resistance) changes many orders of magnitude from a near open circuit to highly conductive, thus clamping the transient voltage to a safe level. The potentially destructive energy of the incoming transient pulse is absorbed by the varistor, thereby protecting vulnerable circuit components. Most electronic systems include varistors in their circuits to protect the components therein from these surges by absorbing them or directing them to ground. Applications range from mobile phones, computers, automotive, aeronautic, spacecraft and electric power lines. Due to the very wide range in size of voltage surges, varistor components are manufactured ranging in size from multi-layered varistors (M.L.V.), disks to arrester blocks (Lee and Kang, 2006; Levinson and Philipp, 1975; Gupta, 1990; Tominaga *et al.*, 1979).

Electrical Characteristics

A typical current-voltage characteristic (I-V) for a ZnO varistor arrester is shown in Figs. 1 and 2. It has three distinctive regions: pre-breakdown, breakdown, and high current. Each region of the curve is important since together they provide for the varistor action associated with surge protection. In the pre-breakdown region, the varistor is resistive at low voltages and the I-V curve is linear (Gupta, 1990). Normal operation of varistors is at the lower voltages within the pre-breakdown region. They are known as the operating and leakage regions during which low currents of microamperes flow through the varistor. This region accounts for the vast majority of a varistor's typical life. The resistance in this region is highly sensitive to temperature (Philipp and Levinson, 1977; Wooi *et al.*, 2013). During normal operation very little heat is generated and the device can operate almost indefinitely. If the temperature of the device is increased for any reason the resistance in the normal operating region decreases thus moving the I-V curve to the right into a higher leakage current range. The pre-breakdown region is the only region that is affected by a high current impulse. Should a surge of a high current pass through the varistor, the resistance in the normal operating region can decrease,

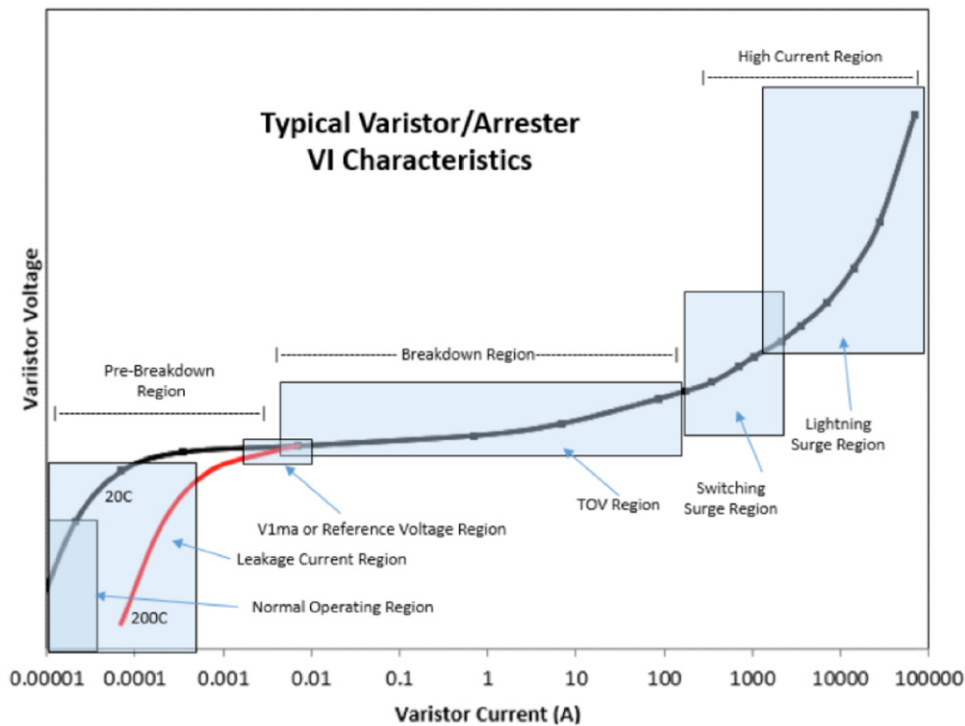


Fig. 1 Typical I-V Characteristics of a ZnO Varistor Surge Arrester. with $I_n = 10$ kA, line discharge class 2. The voltage is normalized to the residual voltage of the ZnO surge arrester at I_n . Reproduced from Woodworth, J., 2019. Understanding arrester VI characteristic curves, Zimmar Holdings Ltd. Available at: <https://www.inmr.com/understanding-arrester-characteristic-curves/>.

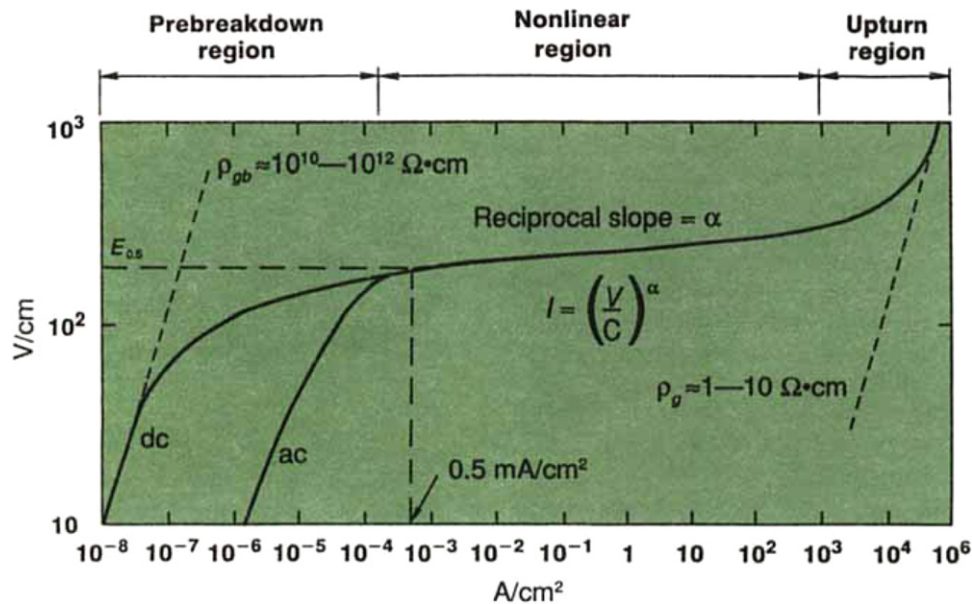


Fig. 2 Typical I-V curve over a wide range of current density and electronic field. Curve is separated into three regions: prebreakdown, nonlinear, and upturn. The dc and ac behavior in the prebreakdown region is also delineated along with the characteristic nonlinear voltage $E_{0.5}$ measured at 0.5 mA cm^{-2} . Reproduced from Gupta, T.K., 1990. Applications of zinc oxide varistors, varistor ceramics. Journal of the American Ceramic Society 73, 1817–1840.

causing more current to flow and possibly failure long after the surge has passed (Woodworth, 2019). Thus, high resistivity combined with maximum stability of the low current characteristics after a surge of high current is very important in this region.

A very important yet the smallest region of the I-V curve is the V1 mA region. It is also known as the breakdown, switching, reference or threshold voltage. It is controlled by the number of junctions or grain boundaries between the electrodes and is often

measured in $V\text{ mm}^{-1}$. Maximum values of $V\text{ mm}^{-1}$ are considered ideal for miniaturization. Its sensitivity to temperature is very small and therefore, at current levels of 1–10 mA, it is used as the reference point from which the rest of the I-V curve can be accurately predicted. This region is the onset of the breakdown region also known as the non-linear region. Above the breakdown voltage the varistor becomes very conductive and the I-V curve is highly non-linear. A dramatic increase in current occurs with a very small increase in voltage. In the breakdown region the I-V characteristic can be simulated by a power law equation (Clarke, 1999; Gadacz *et al.*, 2013):

$$I = KV^\alpha$$

Where K is a proportional factor, α is the non-linearity coefficient, I is the current and V is the voltage. Maximum values of α and longest breakdown regions are most desired (Gupta, 1990). Typical values for α range from 30 to 50. Conductivity in this region is usually caused by power frequency over voltages or transient over voltages (T.O.V.) that can lead to a significant temperature increase in the varistor. Provided that the temperature remains between 100 and 300°C there is no long-term impact on the varistor. It is important that the conductivity in this region cannot last more than a few seconds. Otherwise, it will cause the temperature to rise above the capability of the device.

The high current or upturn region is where the varistor becomes resistive again and a linear relationship between the current and voltage can be seen. It is where the varistor performs its surge clamping function and the resistivity is controlled by the ZnO grains. Here the varistor conducts significant levels of current, greater than 10^3 A (Gupta, 1990). In this region, a dynamic characteristic is observed, wherein the residual voltage is greater for faster current wavefronts (Tominaga *et al.*, 1979; Kim *et al.*, 1996; Brito *et al.*, 2018). The lower part of the high current region is where switching surges are found while above 2000 Amps lightning surges are found (Woodworth, 2019).

A high energy capability is required of ZnO varistors. Based on the literature, approximately 70% of lightning flashes to the ground are multiple strikes with an average number of four strikes per flash, and an average time interval between successive strikes is usually approximately 40 ms. The effects of multiple lightning strike impulse currents on ZnO varistors are cumulative and ZnO varistors are more vulnerable to damage at high-amplitude multiple impulse currents (Bok-Hee and Sung-Man, 2006).

Microstructure of ZnO Varistors

The microstructure of ZnO varistors can be defined as complex, polycrystalline, multiphase, doped semiconducting ceramics (Elfving *et al.*, 2000; Clarke, 1999; Gupta, 1990; Greuter and Blatter, 1990; Levinson and Philipp, 1986; Clark, 1978; Morris, 1973; Santhanam *et al.*, 1979; Inada, 1978).

The non-linear response originates in its polycrystalline microstructure. By proper doping, the near grain boundary region becomes highly resistive while the interior of the ZnO grain becomes conductive, and electrostatic potential barriers build up at the grain boundaries due to charges being trapped at the interface states (Castro *et al.*, 1992; Fernandez-Hevia *et al.*, 2004; Leach, 2005). In this way, varistors are equivalent to back-to-back Zener diodes but with much greater current and energy handling capabilities that make them suitable for high voltage applications.

Sintering of the green compacts takes place in the presence of a liquid phase and the microstructure formed consists of ZnO semiconductor grains with a bismuth rich phase at the single, triple, and multiple junctions that percolates through the whole ceramic body, Table 1, Fig. 3. Fig. 4 shows a scanning electron microscopic image of a ZnO varistor with a commercial composition (Kelleher, 2003). After sintering the primary phase is ZnO, a hexagonal wurtzite crystalline structure, equiaxed in shape and may contain inversion boundaries (IBs). The secondary phases found in the grain boundaries consists of bismuth rich phases which include crystalline precipitates (α , β , γ , and δ), amorphous thin films (1–50 nm), $\frac{1}{2}$ atomic layer of bismuth atoms, (Onreabroy *et al.*, 2006), pyrochlore ($\text{Zn}_2\text{Sb}_3\text{Bi}_3\text{O}_{14}$) and spinel ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$) (Metz *et al.*, 2000). Pores are also evident within and between the ZnO grains (Kelleher, 2003).

The grain boundary includes multiple grain (type I), double ZnO (type II) and single ZnO grain junctions (type III) which is responsible for the I-V characteristics, Fig. 5.

The state of bismuth changes from the triple junction to and along the length of the single ZnO grain junction, Table 2. ZnO varistor materials do not consist of one type of single ZnO-ZnO grain junctions. Three different types have been reported; the first is a continuous bismuth rich film a few nanometers thick (Matsuoka, 1971; Inada, 1978; Kingery *et al.*, 1979), and the second type consists of $\frac{1}{2}$ a monolayer of segregated bismuth ions (Kobayashi *et al.*, 1998; Olsson, 1988a,b; Olsson *et al.*, 1989; Jilsson and Dunlop, 1989a,b). Both types of ZnO-ZnO grain boundaries have different I-V characteristics. A third type of single junction was observed (Morris, 1976; Cerva and Russwurm, 1988; Clark, 1978, 1979) which is devoid of any intergranular phase (atomically abrupt ZnO grain boundaries). Kobayashi *et al.* (1998) attributed the use of the large probe prevented the possibility of observing any bismuth atoms along the single ZnO-ZnO grain boundaries.

Microstructure – Electrical Relationship of ZnO Varistors

Pure zinc oxide is a nonstoichiometric n-type semiconductor with a linear I-V characteristic. The addition of a second phase such as bismuth, barium, praseodymium, neodymium, and vanadium cation (with large ionic radii) oxides, is essential to the formation of a material which has a non-linear region. Multiple dopants such as a combination of antimony, cobalt, manganese, and silicon oxides are added to produce greater non-linearity than the single dopant. During sintering various chemical elements are

Table 1 Summary of the primary phases and features observed in ZnO-Bi₂O₃ commercial varistors along with their characteristics and functions

Phase or feature	Characteristics	Functions
ZnO grains	Bulk of the microstructure. 5–20 μm, equiaxed. Some contain inversion boundaries (IB) or twins. Size influenced by sintering peak temperature, time, and metal oxide additives. TiO₂, Bi₂O₃ and BaO accelerate and SiO₂ and Sb₂O₃ inhibit ZnO grain growth. Wurtzite crystalline structure, oxygen atoms are arranged in a hexagonal close packed type of lattice and zinc atoms occupying half of the tetrahedral sites. Presence of 0.9% Co, 0.3% Mn and 0.3% Ni in solid solution in the ZnO grains.	Size influences the breakdown voltage. Conductivity of the ZnO varistors in the up-turn region of the I-V characteristics and as heat sink for surge energy absorption. The interstitial Zn_i has the fastest diffusion rate and plays a significant role in the stability of the varistor. Concentrations of the dopant elements dissolved in ZnO grains have considerable importance for the electrical characteristics as they strongly influenced the conductivity of the ZnO grains.
Inversion boundaries (IBs)	Straight lines or twin-like structure that bisects almost every ZnO grain. Associated with Sb₂O₃ doping. Pure ZnO have no twins. Neither do ZnO microstructures containing Bi₂O₃.	Associated with antimony doping. Possess potential barriers with higher-than-average breakdown voltages than do the grain boundaries.
Single ZnO-ZnO grain junctions	Bismuth rich film a few nanometers thick. Half atomic layer of segregated bismuth atoms.	The heart of the varistor device. “Good” I-V junctions.
Triple ZnO grain junctions	Amorphous Bi₂O₃. Crystalline Bi₂O₃: α, β, γ and δ-Bi₂O₃ which are monoclinic, tetragonal, body centered cubic and face centered cubic, respectively. Pyrochlore.	Supply of bismuth phase during sintering in the form of liquid phase sintering. Important for grain ZnO grain growth and densification. Maximum grain boundary resistance favors the presence of α-Bi₂O₃, followed by γ and β-Bi₂O₃, and disfavors the presence of the δ-Bi₂O₃ phase because of its highest conductivity.
Spinel	Large spinel phases are between ZnO grains. Small spinel phases are within ZnO grains. Formula Zn₇Sb₂O₁₂ Contains various amounts of chromium, manganese, cobalt, and nickel in solid solution. Appears as faceted octahedral crystals.	Large spinel phases act as grain growth inhibitors during sintering. Small spinel phases in the ZnO grains are too small to provide effective grain boundary pinning and the migrating grain boundaries envelops them, together with a small amount of bismuth rich liquid phase.
Pyrochlore	At the multiple or triple ZnO grain junctions. Formula Zn₂Bi₃Sb₃O₁₄.	Presence not desirable as it introduces easy conduction paths.
Pores	Within and between ZnO grains	Presence not desirable. Non-uniformity in density can cause leakage current to distribute unevenly resulting in a non-uniform temperature distribution. Causes the current density to fluctuate from point to point, resulting in a greater flow of current through the region of least resistance, giving rise to hot spots, increased current channeling through the hot spots, and eventual failure of the device

Note: Reproduced from Olsson, E., 1988a. Developmostructure in ZnO varistor materials. In: Levinson, L.M. (Ed.), Ceramic Transactions Advances in Varistor Technology, The American Ceramic Society, Inc. Westerville, OH, pp. 57–65. Olsson, E., 1988b. Interfacial barriers to electrical conduction in ZnO varistors. In: Levinson, L.M. (Ed.), Ceramic Transactions, Advances in Varistor Technology. Proceedings of the Second International Varistor Conference 3, The American Ceramic Society, Inc. Westerville, OH, pp. 65–73. Eda, K., 1984. Destruction mechanism of ZnO varistors due to high currents. Journal of Applied Physics 56, 2948–2955. Sweetana, A., Radford, K., Johnson, R., Hensley, S., 1989. High-energy metal oxide valve blocks. In: Levinson, L.M. (Ed.), Ceramic Transactions, Advances in Varistor Technology. Proceedings of the Second International Varistor Conference 3, The American Ceramic Society, Inc. Westerville, OH, pp. 240–248.

distributed in such a way in the microstructure that the near grain boundary region becomes highly resistive ($\rho_{gb} \sim 10^{12} \Omega\cdot\text{cm}$) and the grain, g, interior becomes highly conductive ($\rho_g \sim 1\text{--}10 \Omega\cdot\text{cm}$) (Gupta, 1990). These resistivities can be readily estimated from the slopes of the I-V curve. A sharp drop in resistivity from the grain boundary to the grain occurs within about 50–100 nm, known as the depletion layer. At each grain boundary there exists a depletion layer on both sides, extending into the adjacent grains. Varistor action arises because of the presence of this depletion layer within the grains. The presence of two depletion layers on both sides of the grain boundary make the ZnO varistor insensitive to polarity changes. In this respect the varistor appears as a back-to-back diode. Since the region near the grain boundary is depleted of electrons, a voltage drop appears across the grain

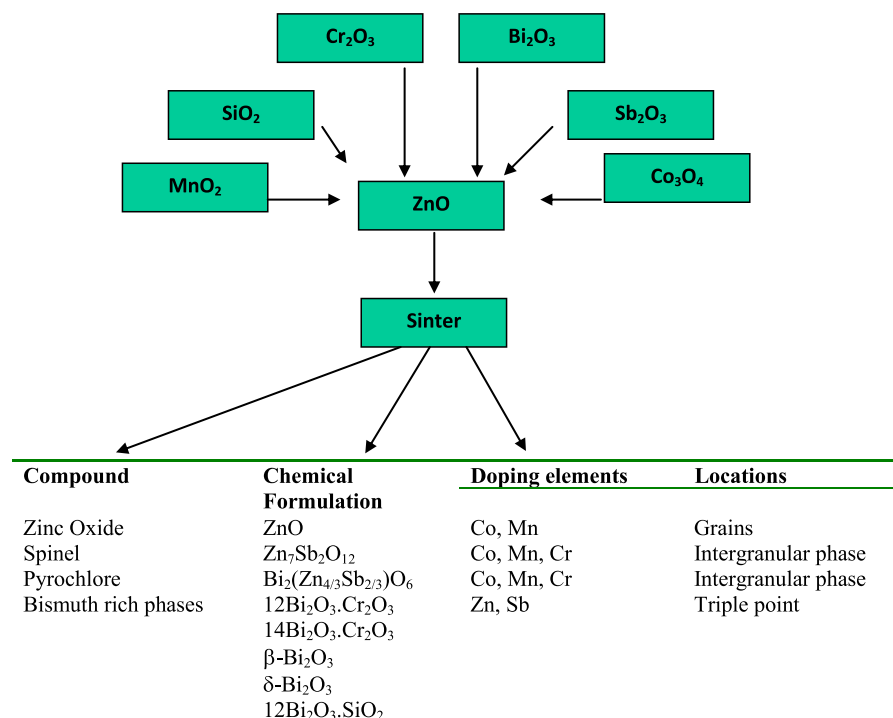


Fig. 3 Microstructural components of the ZnO varistor comprising various crystalline phases, their chemical formulation, and dopants in various phases. Adapted from Gupta, T.K., 1990. Applications of zinc oxide varistors, varistor ceramics. Journal of the American Ceramic Society 73, 1817–1840.

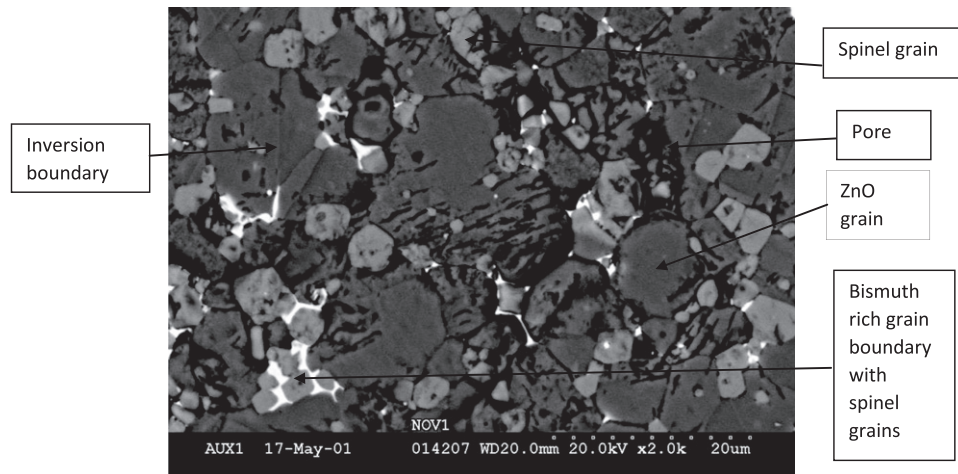


Fig. 4 A back scattered scanning electron microscopic image of a ZnO varistor with a commercial composition. Reproduced from Kelleher, M., 2003. Preparation of Metal Oxide Additive Particles via Mechanical Methods and their Influence on Subsequent Fabrication, Microstructural and Electrical Properties of Commercial ZnO Varistors, (PhD Thesis). Dublin City University.

boundary upon application of an external voltage. This is known as the barrier voltage, V_{gb} and is typically of the order of 3.2 V per grain boundary and is composed of a resistive and a capacitive component. The number of grains in series between the electrodes determines the overall voltage of the varistor device. The low-current pre-breakdown linear region has been identified to be controlled by the grain boundary resistance and capacitance and on the other end of the I-V curve, the high current region ($> 10^3 \text{ A cm}^{-2}$) has been controlled by the impedance of the grain. The intermediate nonlinear region, the region of major importance for a variety of applications, is directly controlled by the resistivity differential between the grain boundary and the grain. Its volume determines the energy of the varistor device. The relationship between the I-V curve to the microstructure of the ZnO varistor provides an important tool to adjust the electrical property of the grain boundary as well as that of the grain to fit the requirements for a given application.

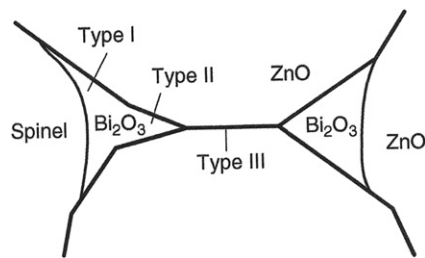


Fig. 5 Schematic arrangement of phases in a ZnO varistor ceramic. Adapted from He, J., 2019. Metal Oxide Varistors, from Microstructure to Macro-Characteristics, Wiley-VCH, Tsinghua University Press. Cerva, H., Russwurm, W., 1988. Microstructure and crystal structure of bismuth oxide phases in zinc oxide varistor ceramics. Journal of the American Ceramic Society 71, 522–530.

Table 2 Summary of the phases observed from the triple junction to the center of the single ZnO–ZnO junction

Section of ZnO grain junction	Composition
Triple ZnO grain junction	Contains the highest concentration of bismuth oxide in both amorphous and crystalline form. The crystalline Bi_2O_3 rich phases tend to be surrounded by an amorphous Bi_2O_3 rich phase. The crystalline bismuth oxide phases consist of a mixture of β and γ - Bi_2O_3 or α - and δ - Bi_2O_3 .
50–40 nm width	Both amorphous and crystalline phases are present. The amorphous phase sandwiched between the crystalline phases and these crystalline phases are in contact with the ZnO grains.
Approximately 15–4 nm width	A crystalline phase exists at only one side of the amorphous phase. Another side of this phase is in direct contact with ZnO grain, indicating that crystalline bismuth oxide phase does not exist at a grain boundary with a width less than 4 nm.
ZnO–ZnO junction less than 4 nm	Only an amorphous bismuth phase observed and is in direct contact with the ZnO grains.
Center of single ZnO–ZnO junction	The existence of continuous segregation of bismuth atoms, $\frac{1}{2}$ an atomic layer.

Note: Kobayashi, K., Wada, O., Kobayashi, M., Takada, Y., 1998. Continuous existence of bismuth at grain boundaries of zinc oxide varistor without intergranular phase. Journal of the American Ceramic Society 81, 2071–2076. Levinson, L., Philipp, H., 1986. Zinc oxide varistors – A review. Ceramic Society Bulletin 65, 639–646. Cerva, H., Russwurm, W., 1988. Microstructure and crystal structure of bismuth oxide phases in zinc oxide varistor ceramics. Journal of the American Ceramic Society 71, 522–530. Inada, M., 1978. Microstructure of non-Ohmic zinc oxide ceramics. Japanese Journal of Applied Physics 17, 673–677. Clark, D.R., 1978. Microstructural location of the intergranular metal oxide phase in a zinc oxide varistor. Journal of Applied Physics 49, 2407–2411. Wang, H., Bartkowiak, M., Modine, F.A., *et al.*, 1998. Nonuniform heating in zinc oxide varistors studied by infrared imaging and computer simulation. Journal of the American Ceramic Society 81, 2013–2022. Elfving, M., Osterlund, R., Olsson, E., 2000. Differences in wetting characteristics of Bi_2O_3 polymorphs in ZnO varistor materials. Journal of the American Ceramic Society 83, 2311–2314.

Effect of Microstructural Disorder

Many techniques used to correlate the electrical behavior with the principal microstructural features led to the realization that varistors are far from uniform (Wang *et al.*, 1998; Hohenberger *et al.*, 1991; Sun *et al.*, 1993; Vojta and Clarke, 1997). Varistors exhibit both microstructural and electrical disorder, which lowers their capability.

Microstructural disorder can be categorised into structural disorder, differences in grain size, crystal orientation, grain boundary structure, uniformity of secondary phases and dopant distribution. The breakdown voltage for a single varistor grain boundary is typically around 3.5 V, with breakdown voltages in polycrystalline devices being estimated according to “brick layer” modules (Leach, 2005). The overall behavior is a summation of the responses of all the grain boundaries. There is considerable evidence for substantial variations in the I–V performance of individual varistor grain boundaries, including differences in breakdown voltage (Olsson *et al.*, 1985; Olsson and Dunlop, 1989a; Olsson *et al.*, 1993; Gupta, 1990; Nan and Clarke, 1996), variations in the shape of the breakdown curve (Tao, 1989) and inactive grain boundaries that do not show the varistor effect at all (Tao *et al.*, 1987; Cao *et al.*, 1994; Tanaka and Takahashi, 1999). Such variability is frequently associated with poorer switching performance and a greater likelihood of device failure because of localized Joule heating, arising from the inhomogeneous responses. The reasons for these differences in grain boundary behaviors are not fully understood (Leach, 2005). Differences in the crystallographic structure of varistors may also affect their electrical behavior brought about by an anisotropic crystal system of ZnO, which is hexagonal (Leach, 2005).

Pores are the other category of disorder that have received less attention. When varistors contain a high percent of porosity the resultant non-uniformity in density can cause the current to distribute unevenly resulting in localized Joule heating (Eda, 1984), greater flow of current through the region of least resistance, hot spots, and eventual failure (Eda, 1984; Sweetana *et al.*, 1989;

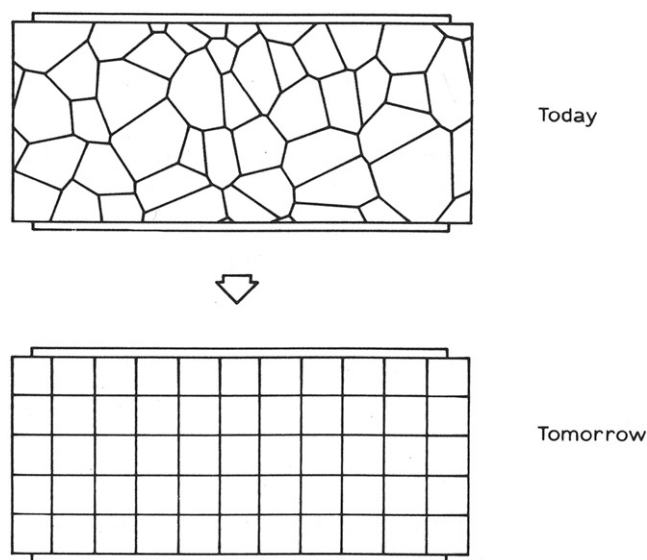


Fig. 6 Localization of the potential barriers – ideal case. Reproduced from Lagrange, A., 1991. Present and future of zinc oxide varistors. In: Steele, B.C.H. (Ed.), *Electronic Ceramics*, Elsevier Applied Science, pp. 185–203.

Wang *et al.*, 1998; Meng *et al.*, 2019). Removal of the hot spots increased the energy absorption capability of the remaining disk by a factor of approximately 3.75 (Sweetana *et al.*, 1989). This result indicates the importance of varistor fabrication in a manner that assures maximum homogeneity and minimum porosity.

The Ideal ZnO Varistor Microstructure

An ideal microstructure was presented by Lagrange (1991), and is shown in Fig. 6. However, in addition to ZnO grains real varistors contain secondary phases, both crystalline and amorphous, and multiple types of grain boundaries. An ideal ZnO varistor has a crystalline microstructure of uniform grain size, shape, and composition as well as minimal presence of mechanical defects such as voids, pores, and cracks (Puyané *et al.*, 1998). The ideal ZnO varistor microstructure should have minimum disorder and maximum uniformity. For maximum energy and peak current capabilities, the ZnO grains should be equiaxed and with a narrow distribution in size. For maximum non-linearity coefficient all the single ZnO-ZnO grain boundary interfaces, perpendicular to the electrodes, should consist of half a monolayer of segregated bismuth atoms. Best low current I-V performance requires that the grain boundaries are resistive. This includes the triple and multiple grain boundaries. The presence of pyrochlore should be avoided. If crystalline bismuth rich phases are to be present in the amorphous bismuth oxide grain boundary, they should be present in the triple or multiple grain boundary junctions and be surrounded by an amorphous bismuth oxide phase. The α - Bi_2O_3 phase is the preferred bismuth rich crystalline phase as it is the most resistive, followed by β - Bi_2O_3 and γ - Bi_2O_3 , and δ - Bi_2O_3 is the least preferred bismuth rich crystalline phase it is the most conductive. The spinel phase, required to control ZnO grain growth, should be in the triple or multiply ZnO grain junctions. The ZnO grains should be free of spinel grains and pores and contain the optimum concentration of cations such as cobalt, manganese etc., in solid solution. Thus, ideal microstructures require maximum density and uniformity and minimum disorder regarding the size, shape, type and distribution of all crystalline and amorphous phases, and pores present.

Methods Investigated & Developed to Achieve the Ideal ZnO Varistor Microstructure

The heart ZnO varistors is the structure (atomic, nano, micro and macro). The composition is the primary factor that determines the structure when sintered and consequently the non-linear characteristics of ZnO varistors, Fig. 7. Once the composition is fixed the process has a significant influence on the microstructure and properties.

Composition

The ZnO varistors is a complex chemical system that contains approximately 90% ZnO and many dopants such as Bi_2O_3 , Sb_2O_3 , CoO , MnO , NiO , and Cr_2O_3 ranging in concentration from parts per million (p.p.m.) to several percent. Dopants play at least three major roles in forming varistors: they can affect grain growth during sintering, the dewetting characteristics of the liquid phase during cooling, and the electronic defect states that control the overall varistor characteristics (He, 2019). The dopant can act as a donor, acceptor, or both, depending on the size of the guest ion, crystal structure of the host lattice, and the relative valency of

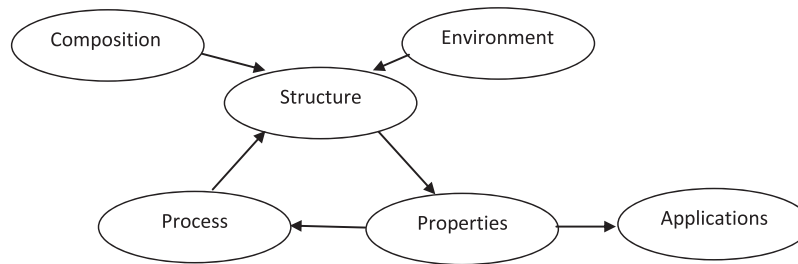


Fig. 7 Relationship between composition, structure, process, properties, and applications of ZnO varistors.

Table 3 Roles of additives on the microstructure and properties of ZnO varistors

Additives	Roles
Bi ₂ O ₃ , Pr ₆ O ₁₁ , V ₂ O ₅ , BaO Sb ₂ O ₃	Varistor makers Inhibits ZnO grain growth, enhances the nonlinearity and breakdown voltage, decreases the leakage current of the varistors, triggers the formation of IBs in ZnO grains.
MnO ₂	Promotes ZnO grain growth, increases the grain boundary resistance, reduces the electrical conductivity of ZnO, helps to build up the potential barrier in the grain boundary, prevents the evaporation of Bi ₂ O ₃ , enhances the nonlinearity.
CoO	Reduces the grain boundary resistivity, leads to the formation of the potential barrier in the grain boundary, enhances the nonlinearity, prevents evaporation of Bi ₂ O ₃ , enhances stability.
Cr ₂ O ₃	Enhances the nonlinearity and the energy absorption capability.
SnO ₂	Forms spinel phase and controls the grain size by triggering the formation of inversion boundaries (IBs) in the ZnO grains.
NiO	Controls the grain size, decreases the leakage current, increases the nonlinear coefficient and breakdown voltage.
CuO	Decreases both the grain and grain boundary electrical conductivities.
TiO ₂	Enhances grain growth, decreases the breakdown field and improves the DC degradation behaviors, triggers the formation of IBs in ZnO grains.
CeO ₂	Inhibits grain growth, enhances the ohmic resistance and breakdown voltage, and reduces the leakage current.
Fe	Improves the nonlinear property and electrical barrier and reduces the electrical conductivity of ZnO as a deep donor.
Al ₂ O ₃ , Ga ₂ O ₃ , or In ₂ O ₃	Reduces the grain resistance to increase the leakage current in the prebreakdown region and decreases the resistivity in the upturn region.
K ⁺ , Li ⁺ , Na ⁺	Controls the grain size, lowers the grain and grain boundary electrical conductivities, decreases the leakage currents, and improves the stability of the varistor.
Ag ₂ O	Reduces grain resistance of ZnO, promotes densification and grain growth of ZnO, increases both the grain and grain boundary resistance in low doping levels, and improves the stability
Rear earth oxides (REO): Pr ₆ O ₁₁ , Y ₂ O ₃ , La ₂ O ₃ , Nd ₂ O ₃ , Er ₂ O ₃ , Ce ₂ O ₃ , Dy ₂ O ₃ and Ho ₂ O ₃	Promotes the pyrochlore-phase formation, controlling different electrical parameters, inhibits grain growth, significantly increases the breakdown field and energy absorption capability, but degradation is accentuated with REO addition.
Ta ₂ O ₅	A small concentration results in high grain conductivity, but excessive Ta ₂ O ₅ decreases both the bulk conductivity and grain size.
WO ₃ , Nb ₂ O ₅	Increases the conductivity of ZnO.
CeO ₂	Inhibits grain growth.
SiO ₂	Inhibits grain growth and increases the nonlinearity.
ZrO ₂	Inhibits ZnO grain growth. (Xie and Hu, 2019)
Y ₂ O ₃	Grain growth inhibitor and increases the nonlinearity of ZnO-Pr ₆ O ₁₁ varistors. (Nahm, 2006)
Boron	Not in He (2019)
V ₂ O ₅	Grain growth inhibitor in low voltage varistors. (Umaru et al., 2016)
	Varistor forming oxides, mainly for low-voltage varistors ZnO-Pr ₆ O ₁₁ varistors. (Nahm, 2006)

Note: Reproduced from He, J., 2019. Metal Oxide Varistors, from Microstructure to Macro-Characteristics, Wiley-VCH. Tsinghua University Press. Anas, S., Mahesh, K.V., Jeon Maria, M., Ananthakumar, S., 2017. Sol-gel materials for varistor devices. In: Pillai, S.C., Hehir, S. (Eds.), Sol-Gel Materials for Energy, Environment and Electronic Applications, Advances in Sol-gel Derived Materials and Technologies, Springer international publishing AG, pp. 23–60.

the guest and host ions. The contribution of each additive has often been considered within a multicomponent system. The performance of a ZnO varistor is a synergistic effect of multiple additives, so it is difficult to investigate the specific role of each dopant in the multicomponent system. The main functions of different additives in ZnO varistors are summarized in Table 3.

Process – Powder Metallurgy

Like all ceramics, because of their lack of plasticity, high melting temperature, and high hardness, ZnO varistors are made using a process known as powder metallurgy (P.M.), **Fig. 8**. It consists of four primary stages; powder preparation, consolidation, sintering and finishing, each of which consists of several sub-stages. In addition to the composition, the microstructure and I-V characteristics of the final varistor device are highly sensitive to the processing stages, substages, their sequence and variables (time, temperature, speed, pressure), the electrode material, the sacrificial materials (organic materials including binders, dispersants, and lubricants) and the indirect materials used in the fabrication process (in equipment including the mill and kiln). Many processing methods have been investigated to improve the microstructure and electrical characteristics, **Table 4**. Powder preparation methods, the focus of this article, has received considerable attention in the literature, followed by sintering.

Powder preparation stage

The characteristics of the powder have a remarkable effect on the subsequent processing, microstructure, and properties ([Rahaman, 1995](#)). Powder preparation methods investigated for ZnO varistors consists of two categories: mechanical and chemical.

Powder properties

The important characteristics of advanced ceramic powders is summarized in **Table 5**. The composition and phases present determine the theoretical density and the electrical properties, i.e., whether varistors are nonlinear or not ([Coulson et al., 1999](#)). The quality (i.e., average and variability) of these properties e.g., percentage of theoretical density and electrical properties are influenced by the physical properties, phase composition and surface characteristics.

Powders consist of an assemblage of small units with certain distinctive physical properties ([Rahaman, 1995](#)). A variety of terms have been used to describe them and a variety of analytical techniques are used to determine their size and morphology. **Fig. 9** is a schematic diagram of an agglomerate consisting of crystallites, primary particles, and pores. The definitions of each unit

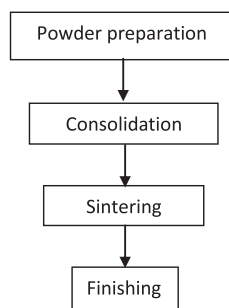


Fig. 8 The four main stages of the Powder Metallurgy Process. Adapted from Puyan , R., 1995. Applications and product development in varistor technology. *Journal of Materials Processing Technology* 55, 268–277.

Table 4 Processing methods investigated to improve the microstructure of ZnO Varistors

Stage	Methods investigated
Powder preparation	Mechanical methods
	Chemical methods
	Drying, freeze and spray
	Calcining
	Organics binders, dispersants, and lubricants
Consolidation	Seeds grains
	Uniaxial, double action compaction
	Isostatic pressing
Sintering	Pressureless sintering, atmosphere, O ₂ , sintering profile, peak temperatures, rate increase and decrease in temperature, temperature stages, two step sintering
	Spark plasma sintering (SPS)
	Hot isostatic pressing (HIP)
	Microwave sintering
	Cold sintering
Finishing	Electrode materials
	Protective layers consisting of either polymer or glass
	Sequence of electrode & protective layer applications

Table 5 Powder characteristics that have a significant influence on processing and microstructure

<i>Chemical composition</i>	<i>Phase composition</i>	<i>Physical characteristics</i>	<i>Surface characteristics</i>
Bulk composition	Phases	Crystal size	Surface structure
Minor elements, %	Single or multiple	Amorphous phase size	Surface chemistry
Trace impurities (p.p.b.-p.p.m.)	Crystalline or amorphous	Particle size	
	Degree of crystallinity	Particle size distribution	
		Particle shape	
		Degree of agglomeration	
		Surface area	
		Internal or closed porosity	
		Open or continuous porosity	

Note: Adapted from Rahaman, M.N., 1995. Ceramic Processing and Sintering, Marcel Dekker, Inc.

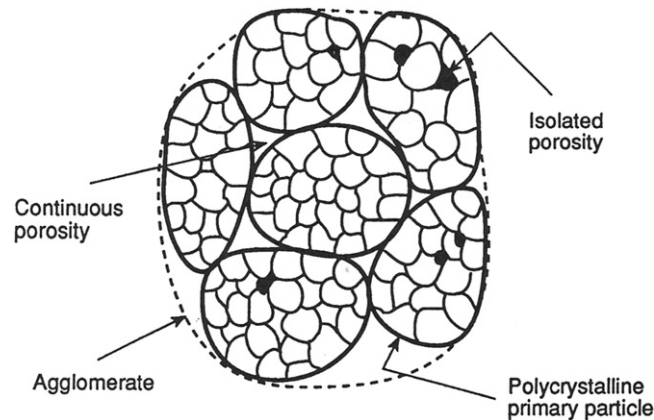


Fig. 9 An agglomerate of ceramic powder particle and primary particles. Adapted from Rahaman, M.N., 1995. Ceramic Processing and Sintering, Marcel Dekker, Inc.

Table 6 Definitions of units within an agglomerate

<i>Unit</i>	<i>Unit definition or description</i>
Primary particles	A discrete, low-porosity unit and can be either a single crystal, a polycrystalline particle, or a glass. If any pores are present, they are isolated from each other. A primary particle cannot, for example, be broken down into smaller units by ultrasonic agitation in a liquid. It is the smallest unit in the powder with a clearly defined surface. For a polycrystalline primary particle, the crystals have been referred to as crystallites, grains, or domains.
Crystallite	It can exist on its own or a subdivision of a primary particle. It can be a single crystal, amorphous or semi-amorphous crystal. It can contain one or multiple elements or molecules.
Agglomerate	A cluster of primary particles held together by surface forces. An agglomerate consists of dense polycrystalline primary particles. Agglomerates are porous, with the pores being generally interconnected. They are classified into two types: soft agglomerates and hard agglomerates. Soft agglomerates are held together by weak surface forces (Van der Waals) and can be broken down into primary particles by ultrasonic agitation in a liquid. Hard agglomerates consist of primary particles that are chemically bonded by solid bridges (ionic or covalent bonds). Hard agglomerates cannot be broken down by ultrasonic agitation in a liquid.
Particles	When no distinction is made between crystallite, primary particle and agglomerate the term particle is used. Particles can be viewed as small units that move as separate entities when the powder is dispersed by agitation and consists of crystallites, primary particles, and agglomerates. Most analytical techniques refer to such particles.
Granules	Refers to large nearly spherical agglomerates ($\sim 20\text{--}1000\text{ }\mu\text{m}$ in size) that are deliberately formed by the addition of a granulating agent (e.g., a polymer-based binder) to the powder, followed by spray or freeze drying. These large, agglomerates improve the flowability of the powder during filling and compaction.
Flocs	Clusters of particles in a liquid suspension.
Colloids	Any system consisting of a finely divided phase in a fluid. A colloidal suspension or sol consists of fine particles dispersed in a liquid. The particles, referred to as colloidal particles, undergo Brownian motion and have a slow (often negligible) sedimentation rate under normal gravity. The size range for colloidal particles is about 1 nm to $1\text{ }\mu\text{m}$.
Aggregates	An aggregate is a coarse constituent in a mixture, which usually also contains a fine constituent called the bond. Hard agglomerates are sometimes referred to as aggregates.
Pores	Pores can be closed and isolated or open and continuous. Closed and isolated pores can exist between the crystallites in a primary particle. Open and continuous pores tend to exist between the primary particles in an agglomerate.

Note: Adapted from Rahaman, M.N., 1995. Ceramic Processing and Sintering, Marcel Dekker, Inc.

Table 7 Analytical techniques used to determine the size of a particle

Method	Range (μm)	Unit within an agglomerate
Microscopy	> 0.5	Agglomerates and primary particles
Optical	> 0.1	Agglomerates, primary particles, and crystallites
Scanning electron (SEM)	> 0.001	Small agglomerates, primary particles, and crystallites
Transmission (TEM)		
Sieving	5–1000	Agglomerates
Sedimentation	0.1–100	Agglomerates and primary particles
Light scattering	0.1–1000	Agglomerates and primary particles
Zeta-sizer	< 0.001	Agglomerates and primary particles
X-ray line broadening	< 0.1	Crystalline crystallite
Specific surface area	–	Obtained by calculation with the assumption that the surface area measured is that of a powder consisting of individual and isolated spherical units.

Note: Adapted from Rahaman, M.N., 1995. Ceramic Processing and Sintering, Marcel Dekker, Inc.

Table 8 Ideal powder characteristics for ZnO varistors

Powder characteristic	Desired property
Particle size	Fine (nano-meter - submicron)
Particle size distribution	Narrow
Particle shape	Spherical or equiaxial
Stage of agglomeration	No agglomeration (hard or soft) or soft agglomerates
Chemical composition	High purity
Phase composition	Single phase
Surface area	High
Internal or closed porosity	None
Surface	Uniform and highly pure

Note: Adapted from Rahaman, M.N., 1995. Ceramic Processing and Sintering, Marcel Dekker, Inc.

within the agglomerate are in [Table 6](#). The analytical techniques used to determine the size of a particle are summarized in [Table 7](#). [Table 8](#) summarises the ideal powder characteristics required for ZnO varistors.

Ideal powder properties for ZnO varistors

Ideal ZnO varistor powders serve two functions. The first is to achieve the ideal microstructure and thus properties when the green body has been sintered and the second is to encourage reproducible fabrication with a resulting varistor with a reliable performance.

To achieve a uniform sintered microstructure a uniform green microstructure consisting of uniformly packed particles with a narrow distribution in size is needed ([Bowen, 1984](#)). Ideal powders are characterized by particles which are equiaxed, sub-micrometer (nanometer) in size, absence of particle aggregates, narrow size distribution (mono-size), and high chemical purity ([Segal, 1991](#)). Ideal varistor powders also require that all the dopant elements must be as homogeneously mixed as possible. Particle size is particularly important in that it affects properties such as the surface area, the rate at which the particle settle in a fluid, chemical reactivity, densification, grain size, grain size distribution and uniformity of each phase. Densification of fine particles is profoundly greater than that of coarse particles. During sintering of a green body, a highly homogeneous composition is desired so that all diffusion distances are equal, allow the formation of all the initial phases in one burst (depends also on the uniformity of the temperature), grow uniformly, and densification occurs fully and uniformly. When sintering has ended all the ZnO grains should be similar in size, shape, orientation and homogeneous in composition of dopants, the secondary phases are uniformly distributed, similar in size, shape, in the right location and contain a homogeneous distribution of dopants, and the fired body contains zero pores, i.e., the ideal microstructure.

Reproducible fabrication of varistors with reliable performance require more from powders. On an industrial scale, large quantities of particles are handled ([Coulson et al., 1999](#)) in important operations like drying, calcining, storage in hoppers, flow through orifices and pipes, and into compaction equipment. It is necessary to form particles into soft agglomerates with desirable properties (uniform size and composition of organic, inorganic materials, and moisture) by processes like spray or freeze drying. Hard agglomerates or aggregates must be avoided completely.

Powders of high purity are also required. Impurities on the surface of powders may have a significant influence on the dispersion of the powder in a liquid ([Coulson et al., 1999](#)) and may lead to the presence of a small amount of another phase,

which can cause selected growth of individual grains during sintering. The achievement of fine and uniform grain size would be impossible.

Powder preparation methods investigated

Mechanical and chemical methods have been investigated to prepare powders for ZnO varistors, [Table 9](#).

The conventional or mixed oxide method, [Fig. 10](#), for producing ZnO varistors powders is ball milling, though which milling method is often not stated. Multicomponent oxide varistor powders are made by blending oxides, hydroxides, or carbonates after which the mixture is milled (usually wet) and dried by placing in an oven or agglomerated by spray or freeze drying. Ovens are mostly used in laboratory research. In industry, as powders are handled on a large scale, drying is mostly achieved by spray agglomeration to form powders that retain their uniformity in composition from the blending stage, flow easily, and uniformly to the next stage. After the drying stage two approaches are taken. The first approach, mostly reported in the literature, is where the dried powder is then compacted and sintered. The second approach is where the dried powder is calcined, followed by a second milling and a second drying stage. Afterwards the dried powder is compacted and sintered. Repeated milling and calcining are used

Table 9 Powder preparation methods investigated and developed for ZnO varistors

Powder preparation methods	Advantages	Disadvantages
Mechanical methods Comminution or milling tumbling ball, vibratory, attrition, planetary, high energy, cryogenic. Prior preparation of the constituent phases.	Inexpensive Wide applicability Wider range of metal oxide suppliers Wider range of particle sizes including nanometer	Limited purity Limited homogeneity Large particles if used.
Chemical methods - liquid solutions Precipitation or coprecipitation: Solvent vaporization (spray drying, spray pyrolysis, freeze drying, sol-gel), & metal organic polymeric methods, microemulsion) Combustion	High purity, Small particles, Composition control, Chemical homogeneity.	Expensive, Large quantities of liquid required, Large number of extra stages required, Powder agglomeration is usually a problem.

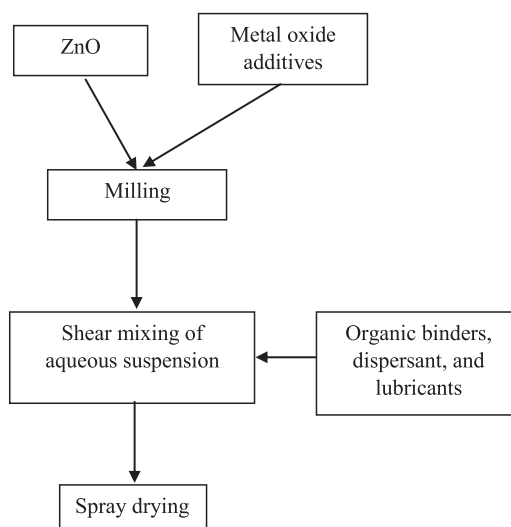


Fig. 10 Sub-stages in the conventional or mixed oxide method for preparing powders ready for consolidation or compression of ZnO varistors. Reproduced from Kelleher, M., 2003. Preparation of Metal Oxide Additive Particles via Mechanical Methods and their Influence on Subsequent Fabrication, Microstructural and Electrical Properties of Commercial ZnO Varistors, (PhD Thesis). Dublin City University. Anas, S., Mahesh, K.V., Jeen Maria, M., Ananthakumar, S., 2017. Sol-gel materials for varistor devices. In: Pillai, S.C., Hehir, S. (Eds.), Sol-Gel Materials for Energy, Environment and Electronic Applications, Advances in Sol-gel Derived Materials and Technologies, Springer international publishing AG, pp. 23–60.

to enhance the homogeneity of the powder. These two approaches are used for producing varistor disks and arrestor blocks. To produce multi-layered varistors (MLV) screen printing is the consolidation method used.

Mechanical methods

Mechanical methods investigated include ball milling, prior preparation of the constituent phases and seeds. ZnO seed crystals are used to obtain varistors with low voltage. Milling, prior preparation of the constituent phases and chemical methods have been investigated to produce high voltage varistors.

Ball milling (ball, vibratory, attrition, planetary, high energy) of metal oxides

The purpose of milling is to reduce the particle size, increase the surface area, and intimately mix the metal oxide additives together with the aqueous or non-aqueous liquids, organic material if present, without the introduction of impurities, to achieve maximum density and homogeneity in the final microstructure of the sintered device, **Table 10**. With the advancement of new high energy milling methods, the electrical and microstructural properties reported are comparable to many of those obtained from chemical methods (**Tables 14** and **15**). Ball mills investigated for ZnO varistor powders include tumbling, vibratory, attrition, planetary, high energy, and cryogenic mills. The rate of particle size reduction depends on the mill parameters (diameter, speed), the properties of the milling media (size, hardness, density, shape), and the properties of the particles to be ground. Generally, ball mills that run at low speeds contain large balls because most of the mechanical energy supplied to the particle is in the form of potential energy. Those that run at high speeds contain small balls, with as high a density as possible, because most of the energy supplied to the particle is in the form of kinetic energy. The choice of the grinding medium is usually limited by cost, wear rate and wear material.

Milling has been shown to be an integral part of the process of preparing powders for ZnO varistors whether the powder is prepared from mixing of the individual metal oxides (Kelleher, 2003; Kelleher and Hashmi, 2008, 2011), nano to micron size particles, including, and excluding ZnO powder (McArdle, 1995; McArdle *et al.*, 1995), prior preparation of the individual phases (Branković *et al.*, 2000, 2007; Žunić *et al.*, 2007; Bernik *et al.*, 2008), or from a chemical route (Pillai *et al.*, 2008).

Many different milling methods with a wide range of media materials and speeds have been investigated, **Tables 11** and **12**. The effect of several milling methods, ball (McArdle *et al.*, 1995), vibratory (Kelleher and Hashmi, 2008), attrition (Kelleher, 2003), horizontal sand milling (Yan *et al.*, 2020), on the particle size, D50, of the mixed metal oxide dopant additives that were determined by laser diffraction and summarized in **Fig. 11**. The efficiency of milling is determined by both the milling method, and the size and morphology of the original metal oxide powders. Vibratory and attrition milling are more efficient than ball milling. Within two hours the original average particle size was reduced to less than a micron. Horizontal sand milling reduced the average particle size from 760 nm to 152 nm within one hour.

Table 10 Relationship between particle size reduction and the effect on fabrication and microstructural characteristics

Powder characteristics		Fabrication characteristics	Microstructure characteristics
Particle Size Reduction	Increases mixing	Increases chemical reactivity and phase transformation	Decreases grain size distribution and increases phase uniformity
	Increases specific surface area	Increases Densification, Chemical Reactivity and Phase Transformation	Lowers sintering temperature, Increases density
	Decreases porosity between particles	Increases uniformity of densification	Decreases porosity, pore size & distribution in size, increases density.
	Separates inter-particle chemical constituents	Increases mixing of chemical and phase constituents, and thus chemical reactivity and densification	Increases phase uniformity

Note: Reproduced from Kelleher, M., 2003. Preparation of Metal Oxide Additive Particles via Mechanical Methods and their Influence on Subsequent Fabrication, Microstructural and Electrical Properties of Commercial ZnO Varistors, (PhD Thesis). Dublin City University.

Table 11 Comparison of different ball mills.

Mill type	Horizontal or Vertical	Media shape	Media size (mm)	Revolutions per minute (r. pm.)	Volume of mill occupied by media (%)
Ball (tumbling) mill	Horizontal or at a small angle and chamber rotates	Sphere or cylindrical	20 and larger	10–50	30–50
Vibratory mill	Vertical	Cylindrical	20 * 10	6–60 Hz in 3 dimensions	80–90
Attritor	Vertical or horizontal	Sphere	0.3–10	60–350	80–90
High-speed attritor	Horizontal	Spheres	0.5–3	320–1700	80–90
Sand Mill/Horizontal Mill	Vertical or horizontal	Spheres	0.25–2	800–3800	80–90
Planetary mill	Vertical	Spheres	0.25–20	500–1000	80–90

Note: (Adapted from Union Process).

Table 12 Ball milling methods and parameters used for fabrication of ZnO-Bi₂O₃-Sb₂O₃ varistor powders

<i>Milling method</i>	<i>Supplier</i>	<i>Speed (rpm)</i>	<i>Mill lining material</i>	<i>Media material</i>	<i>Media diameter (mm)</i>	<i>Powder: Media (mass)</i>	<i>Wear (ppm)</i>	<i>Author</i>
Tumbling ball	Lab size	–	PE	ZrO ₂	Cylinders D*h 20 * 10		–	McArdle (1995)
Vibratory	Sweeco Ind. M18	80 Hz	PU	ZrO ₂	Cylinders D*h 20 * 10	5 kg:8 litres	Zr	Kelleher (2003), Kelleher and Hashmi (2008, 2011)
Attrition	Dyno mill model KDL	1000	Nylon	YTZ Tosoh	1		Zr	Kelleher (2003)
High energy shaker	–		Ceramic	Steel	20	–	–	Fah and Wang (2000)
High energy shaker	SPEX™ model 8000-D		SS	–	5	1:10	Fe	Gómez-Yáñez <i>et al.</i> (2004)
Horizontal oscillatory	Retch, MM2	25 Hz	–	–	–	–	–	Damonte <i>et al.</i> (2004)
Horizontal sand	–	80	–	–	–	–	–	Yan <i>et al.</i> (2020)
Planetary	–	700	Steel	–	–	–	–	Alamdari <i>et al.</i> (2000)
Planetary	–	500	Nylon	ZrO ₂	–	1:20	–	Hongyu <i>et al.</i> (2007)
Planetary	–	500	Nylon	SS	–	1:20	–	Liu <i>et al.</i> (2007)
Planetary	–	500	PE	ZrO ₂	–	1:20	–	Dong <i>et al.</i> (2012)
Planetary	–	800	Nylon	Steel	–	–	–	Zhu <i>et al.</i> (2012)
Planetary	–		Agate	Agate	20	1:20	–	Branković <i>et al.</i> (2007)
Planetary	–	66	Agate	Agate	20	1:7	–	Žunić <i>et al.</i> (2007), Bernik <i>et al.</i> (2008)
		340				1:20		
Planetary	–	–	–	ZrO ₂	–	–	–	Chen <i>et al.</i> (2021)

PU: Polyurethane, PE: Polyethylene, ZrO₂: Zirconia, YTZ: yttrium stabilized zirconia, Tosoh Europe B.V., SS: Stainless steel, D*h: Diameter*height, rpm: revolutions per minute, ppm: parts per million.

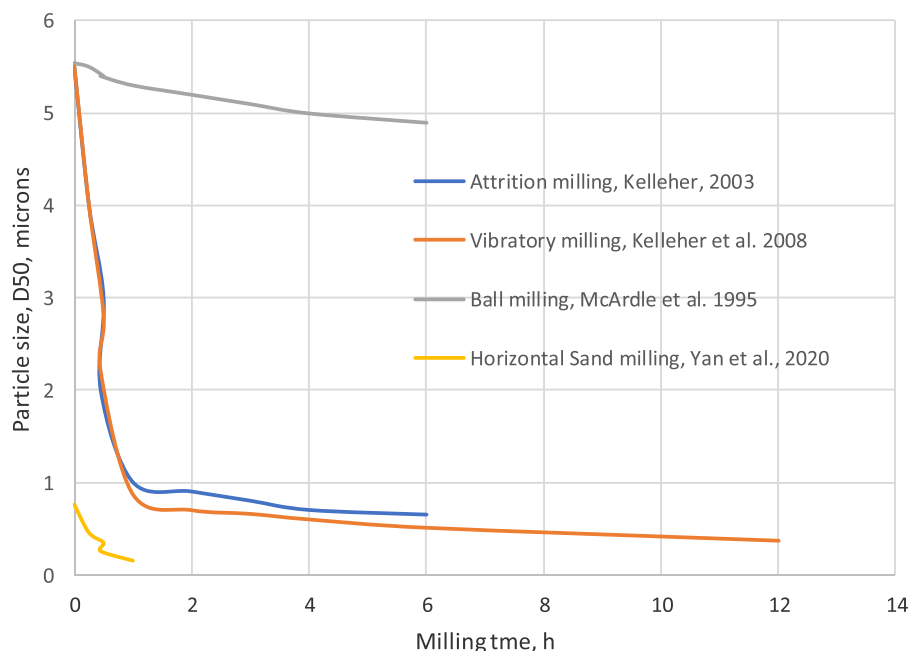


Fig. 11 The effect of different milling methods and durations on the average particle size, D50, of the metal oxide dopants as determined by laser diffraction.

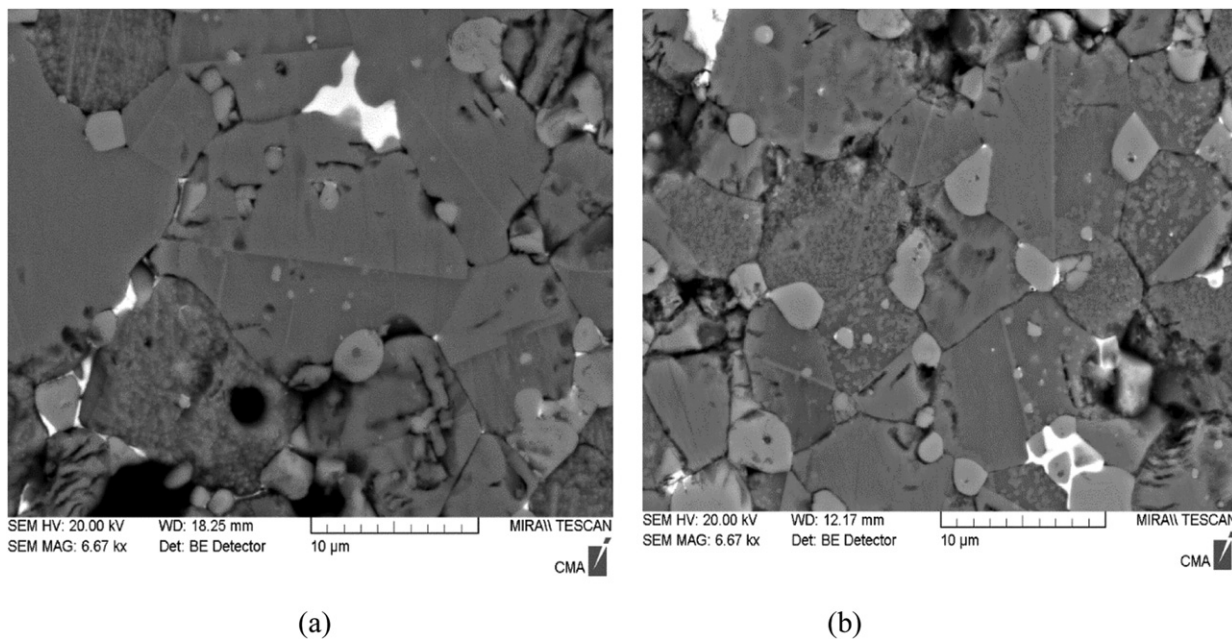


Fig. 12 Back scattered scanning electron microstructures of sintered varistors made from powders which were vibratory milled for (a) 0 h and (b) 12 h. Reproduced from Kelleher, M., 2003. Preparation of Metal Oxide Additive Particles via Mechanical Methods and their Influence on Subsequent Fabrication, Microstructural and Electrical Properties of Commercial ZnO Varistors, (PhD Thesis). Dublin City University.

With the development of high energy milling technology, a large interest followed in the use of high energy shaker (Fah and Wang, 2000; Gómez-Yáñez *et al.*, 2004), horizontal oscillatory (Damonte *et al.*, 2004), horizontal sand (Yan *et al.*, 2020) and planetary ball mills (Hongyu *et al.*, 2007; Liu *et al.*, 2007; Žunić *et al.*, 2007; Dong *et al.*, 2012; Zhu *et al.*, 2012) to reduce the particle size and mix the metal oxides powders. Planetary ball milling was also used with nano ZnO particles (Chen *et al.*, 2021) and in the prior preparation of constitutional phases (Branković *et al.*, 2000; Branković *et al.*, 2007; Žunić *et al.*, 2007; Bernik *et al.*, 2008). A wide range of milling durations, speeds, media size, media material and media to powder ratio, lining materials were used, Table 9.

All milling methods investigated showed a large effect on the properties of the powders and consequently on the microstructure and electrical properties of the varistors obtained. After 12 h of vibratory milling the average size of the mixed metal oxide additives decreased from greater than 5 μm to less than 0.4 μm , Fig. 14, (Kelleher, 2003; Kelleher and Hashmi, 2008, 2011). Using a horizontal sand mill, within 60 min the average particle size decreased from 0.760 to 0.152 μm , the viscosity increased from 857 to 14,600 mPa.s and the Zeta potential decreased from -35.9 to -13.0 mV (Yan *et al.*, 2020). The specific surface area increased after 10 h of milling from 2.3 to 5.9 $\text{m}^2 \text{g}^{-1}$ using a high energy shaker mill, (Fah and Wang, 2000) and from 4 to 40 $\text{m}^2 \text{g}^{-1}$ using a planetary ball mill (Alamdari *et al.*, 2000), which is equivalent to those reported for chemically derived varistor powders. After 20 h the concentration of iron was 1.39 wt% using a planetary mill and stainless-steel media (Liu *et al.*, 2007). Despite the increase in the amount of iron the low current electrical characteristics, V_B , α and I_L , improved with increasing milling duration, Table 14.

The characteristics of microstructure were influenced by the milling methods investigated. As the duration of vibratory milling of the dopants (Kelleher, 2003) and the intensity of planetary milling increased (Žunić *et al.*, 2007) the mean and distribution in the ZnO grain size decreased, the uniformity of both the bismuth and antimony rich phases increased, the concentration ZnO grains containing IB increased, and both the mean and distribution of the size of the spinel grains decreased, Fig. 15. Increased vibratory milling duration improved the bismuth phase dispersion throughout the microstructure, thus improving its availability to form the single ZnO-ZnO grain junctions which is responsible for the varistor action. Planetary milling was even more effective. Increasing the intensity of planetary milling increased the availability of Sb_2O_3 from the spinel phase to form IBs, increased the

Table 13 Composition of the three phases

Phase	Composition
Doped ZnO	99.8 mol% ZnO + 0.2 mol% ($\text{Co}^{2+} + \text{Mn}^{2+}$)
Doped spinel	$\text{Zn}_{1.971}\text{Ni}_{0.090}\text{Co}_{0.030}\text{Cr}_{0.247}\text{Mn}_{0.090}\text{Sb}_{0.545}\text{O}_4$
Doped bismuth, $\gamma\text{-Bi}_2\text{O}_3$	$6\text{Bi}_2\text{O}_3\text{MnO}_2$

Note: Reproduced from Branković, Z., Branković, G., Bernik, S., Žunić, M., 2007. ZnO varistors with reduced amount of additives prepared by direct mixing of constituent phases. Journal of the European Ceramic Society 27, 1101–1104.

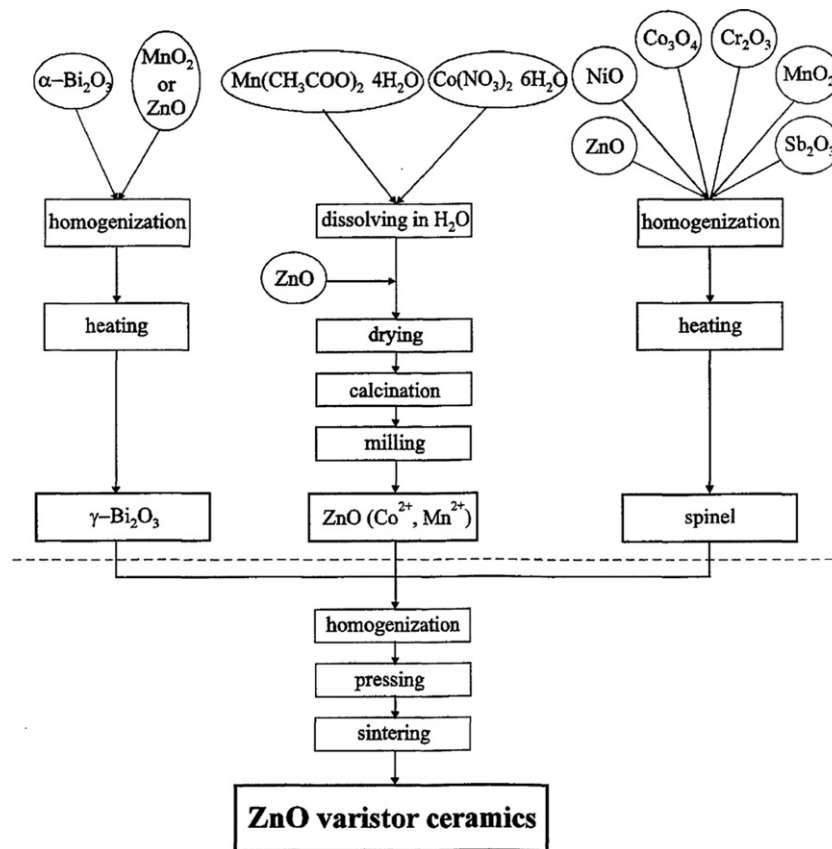


Fig. 13 A schematic presentation of the method used to prepare the ZnO varistor ceramics. Reproduced from Branković, Z., Milošević, O., Poleti, D., Karanović, L., Uskoković, D., 2000. ZnO varistors prepared by direct mixing of constituent phases. Materials Transactions JIM 41, 1226–1231.

Table 14 The effect of milling method and time on the powder, electrical and microstructural properties of ZnO-Bi₂O₃-Sb₂O₃ based varistors

Mechanical method	Author (year)	ZnO varistor dopants	Milling time	Particle size, (nm)	Sinter temperature (°C)	T.D. (%)	Average grain size (μm)	E _b (V mm ⁻¹)	α	J _L (μA cm ⁻²)
Different ball milling methods of metal oxide dopants – effect of milling duration.										
Vibratory milling	Kelleher (2003) and	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ ,	0 h	5,500 (L.D.)	1150	>98	13.55	168	25.4	-
Zirconia media	Kelleher and Hashmi	SnO ₂ , NiO.	6 h	510 (L.D.)		>98	11.68	198	26.5	-
Mixed oxide dopants	(2008)		12 h	370 (L.D.)		>98	11.66	205	27.3	-
High energy shaker mill	Fah and Wang (2000)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO.	0 h	450 (B.E.T.)	1100	98	~7	310	17	-
			10 h	170 (B.E.T.)		99.5	~4	440	240	-
	Gómez-Yáñez <i>et al.</i> (2004)	Sb ₂ O ₃ , Bi ₂ O ₃ .	0 h	-	1200	>94	-	76	7.3	-
			3 h	-		>98	-	161	5.8	-
High energy ball mill	Alamdari <i>et al.</i> (2000)	-	0.5 h	-	1000	5.3 g cm ⁻³	4 (0–10)	800	-	-
			10 h	-		5.8 g cm ⁻³	2 (0–5)	1250	~ 59	-
Planetary ball mill	Žunić <i>et al.</i> (2007)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , NiO, Cr ₂ O ₃ .	Metal Oxides Unmilled	-	1200	92	6.3	268	41	19.2
			Metal Oxides Intensively milled	-		94	3.51	441	46	12.4
	Liu <i>et al.</i> (2007)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , Cr ₂ O ₃ .	Milling 0 h	120 (XRD)	900	< 94	-	900	22	~0
			Milling 20 h	59 (XRD)		98.5	-	420	17	~0
	Hongyu <i>et al.</i> (2007)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , Cr ₂ O ₃ , NiO.	Milling 5 h	-	800	5.14 g cm ⁻³	1.6	890	51	0.16
	Dong <i>et al.</i> (2012)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , Cr ₂ O ₃ .	Milling 0 hr	-	1000	97	-	510	30	~0
			Milling 3 h	-		95	-	617	57	~0
	Zhu <i>et al.</i> (2012)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , Cr ₂ O ₃ , NiO, SiO ₂ , Pr ₆ O ₁₁ , Al- NO ₃ H ₃ BO ₃ , AgNO ₃ .	Milling 0 h	0.01–6 μm (Z.S.)	1075	5.28 g cm ⁻³	7.2	363	67	1.08
			Milling 10 h	0.01–4 μm (Z.S.)		-	5.1	565	75	0.45
			Milling 20 h	0.01–3 μm (Z.S.)		5.71 g cm ⁻³	4.0	650	74	0.58
Horizontal sand milling	Yan <i>et al.</i> (2020)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , NiO, Ag glass	Milling 0 h	760 (L.D.)	1050	5.52 g cm ⁻³	5.75	260	22.5	4.3
			Milling 30 min	347 (L.D.)		5.58 g cm ⁻³	3.41	310	32.7	1.0
Prior preparation of constitutional phases.										
Planetary ball mill	Branković <i>et al.</i> (2000)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , NiO, Cr ₂ O ₃ .	3 phases milled	5 μm	1100	99	~10	~ 450	35	<0.1 A m ⁻² (80% V _B)
Doped ZnO, spinel and γ-Bi ₂ O ₃ (70:20:10 mass%)										
Planetary ball mill	Branković <i>et al.</i> (2007)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , NiO, Cr ₂ O ₃ .	Unmilled 3 phases	-	1030	90	-	484	46	4.1
Doped ZnO, spinel and γ-Bi ₂ O ₃ (85:10:5 mass%)			Intensively milled 3 phases	-		91	-	824	53	2.3
Planetary ball mill			Unmilled 3 phases	-		89	-	443	38	49.6
Doped ZnO, spinel and γ-Bi ₂ O ₃ (92.5:5:2.5 mass%)			Intensively milled 3 phases	-		98	-	527	50	5.6

(Continued)

Table 14 Continued

Mechanical method	Author (year)	ZnO varistor dopants	Milling time	Particle size, (nm)	Sinter temperature (°C)	T.D. (%)	Average grain size (μm)	E _b (V mm ⁻¹)	α	J _L (μA cm ⁻²)
Planetary ball mill Doped ZnO, spinel and γ-Bi ₂ O ₃ (85:10:5 mass %)	Žunić <i>et al.</i> (2007)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , NiO, Cr ₂ O ₃ .	Unmilled 3 phases	-	1200	95	5.92	437	50	4.5
			Intensively milled 3 phases	-		98	2.99	895	53	2.5
Planetary ball mill Doped ZnO, spinel and γ-Bi ₂ O ₃ (92.5:5:2.5 mass%)	Bernik <i>et al.</i> (2008)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ , NiO, Cr ₂ O ₃ .	Unmilled 3 phases	-	1100	89	4.4	443	38	10
			Intensively milled 3 phases	-		98	4.0	527	50	6
Nano ZnO particles.	Chen <i>et al.</i> (2021)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₂ O ₃ , MnO ₂ , Cr ₂ O ₃ , Y(NO ₃) ₃ ·6H ₂ O, Al (NO ₃) ₃ ·6H ₂ O.	30 nm ZnO	-	1100	96	1.39	859	29.4	2.98
Planetary ball mill			50 nm ZnO	-		97	1.42	962	36.8	2.76
			90 nm ZnO	-		99	1.46	1015	37.9	2.45
			500 nm ZnO	-		95	1.46	810	34.3	2.45
Nano-filled varistor nanorod particles.										
Mixture of commercial spray dried mixed metal oxide powder with chemically prepared powder.										
Wet mixed mechanically	Anas <i>et al.</i> (2013)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , Cr ₂ O ₃ .	Commercial powder	40 nm (XRD) 2 m ² g ⁻¹ (BET)	1100	5.57 g cm ⁻³	8 (max.)	421	17	-
			Mixed commercial + chemical powder (5%)			5.58 g cm ⁻³	2.8 (max.)	875	31	-
			Chemically prepared powder	20 nm (XRD) 22 m ² g ⁻¹ (BET)		5.41 g cm ⁻³	4.6 (max.)	450	11	-

T.D.: Percent of theoretical density, I_L : leakage current density at 75% of the breakdown voltage, E_b : breakdown voltage at 1 mA.cm⁻², α : coefficient of nonlinearity (1–10 mA cm⁻²), J_L (μA cm⁻²): Leakage current is measured at the voltage of 0.8 K₀, D: average ZnO grain size, S.D.: percent standard deviation in grain size. L.D.: Laser diffraction, Z.S.: ZetaSizer, XRD: X-ray diffraction, T.E.M.: Transition electron microscope, BET: Brunauer, Emmett and Teller, Max.: maximum, SPS: Spark Plasma Sintering.

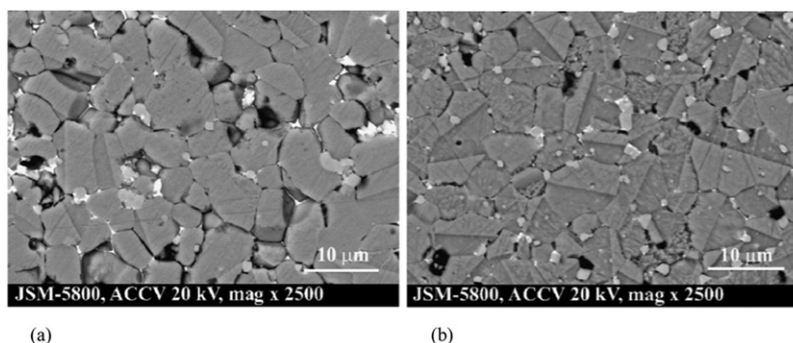


Fig. 14 SEM of the polished and chemically etched surfaces of the sintered varistor samples ($\text{ZnO:Spinel}:\gamma\text{-Bi}_2\text{O}_3$ 92.5:5:2.5): (a) “unmilled” sample 3 phases, and (b) intensely milled 3 phases. All samples were sintered at 1200°C for 1 h. Reproduced from Žunić, M., Branković, Z., Bernik, S., Góes, M.S., Branković, G., 2007. ZnO varistors from intensively milled powders. *Journal of the European Ceramic Society* 27, 3897–3900.

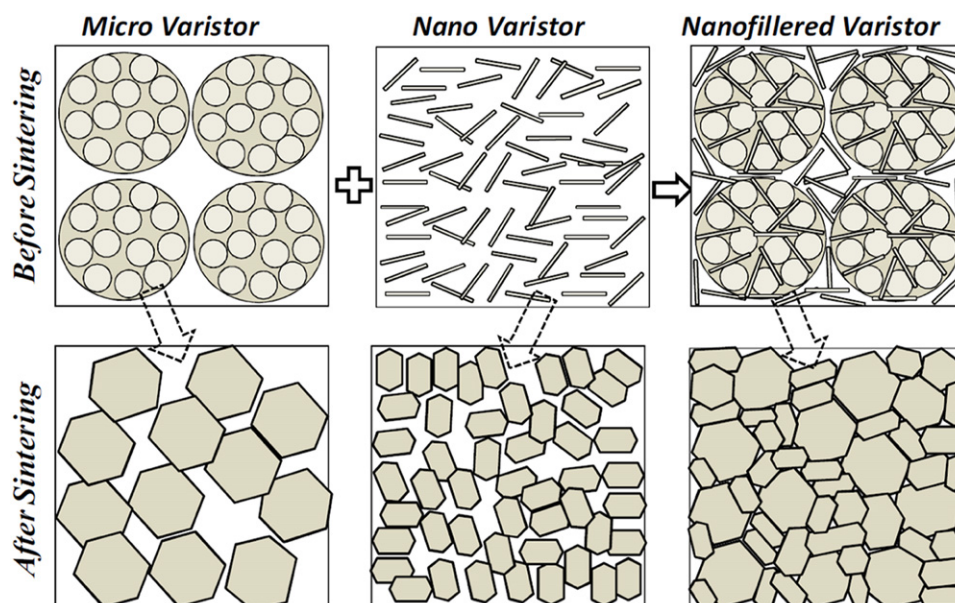


Fig. 15 Schematic representation of the “nano-micro composite” or “nanofilling” approach. Reproduced from Anas, S., Mahesh, K.V., Jobin, V., Prasanth P., Ananthakumar, S., 2013. Nanofillers in ZnO based materials: A ‘smart’ technique for developing miniaturized high energy field varistors. *Journal of Materials Chemistry* 1, 6455–6462.

number of defects in the ZnO grains which contributed to the enhancement of IBs nucleation, decreased the ZnO grain size $< 10\ \mu\text{m}$, reduced the ZnO grain size distribution, and reduced the amount of porosity (Žunić *et al.*, 2007) (Fig. 12).

With increasing duration and intensity of milling the breakdown voltage and the nonlinearity coefficient increased, and the leakage current decreased, Table 14. (Fah and Wang, 2000; Gómez-Yáñez *et al.*, 2004; Damonte *et al.*, 2004; Yan *et al.*, 2020; Hongyu *et al.*, 2007; Liu *et al.*, 2007; Žunić *et al.*, 2007; Dong *et al.*, 2012; Zhu *et al.*, 2012). Higher increases in the breakdown voltages and nonlinearity coefficients were, in general, reported for planetary milling than vibratory milling. The stability of the low current characteristics after pulsing at 65 kV also improved with vibratory milling duration (Kelleher, 2003).

The peak sintering temperature had the greatest effect on the electrical properties followed by the duration of planetary milling (Dong *et al.*, 2012). Highest breakdown voltages, $900\text{--}1400\ \text{V mm}^{-1}$, were obtained for samples sintered at 900°C , and reduced to $300\text{--}400\ \text{V mm}^{-1}$ when sintered at 1100°C . The breakdown voltage increased with increasing milling time, the lower the sintering temperature the higher the effect of milling duration. This effect also seen with the sinter density, low current leakage, and nonlinearity coefficient. The optimum density and electrical characteristics were achieved when sintered at 1000°C and milled for 1 h where the density, breakdown voltage, nonlinear coefficient and low current leakage were 95.5%, $\sim 450\ \text{V mm}^{-1}$, 57 and close to 0 respectively, Table 14.

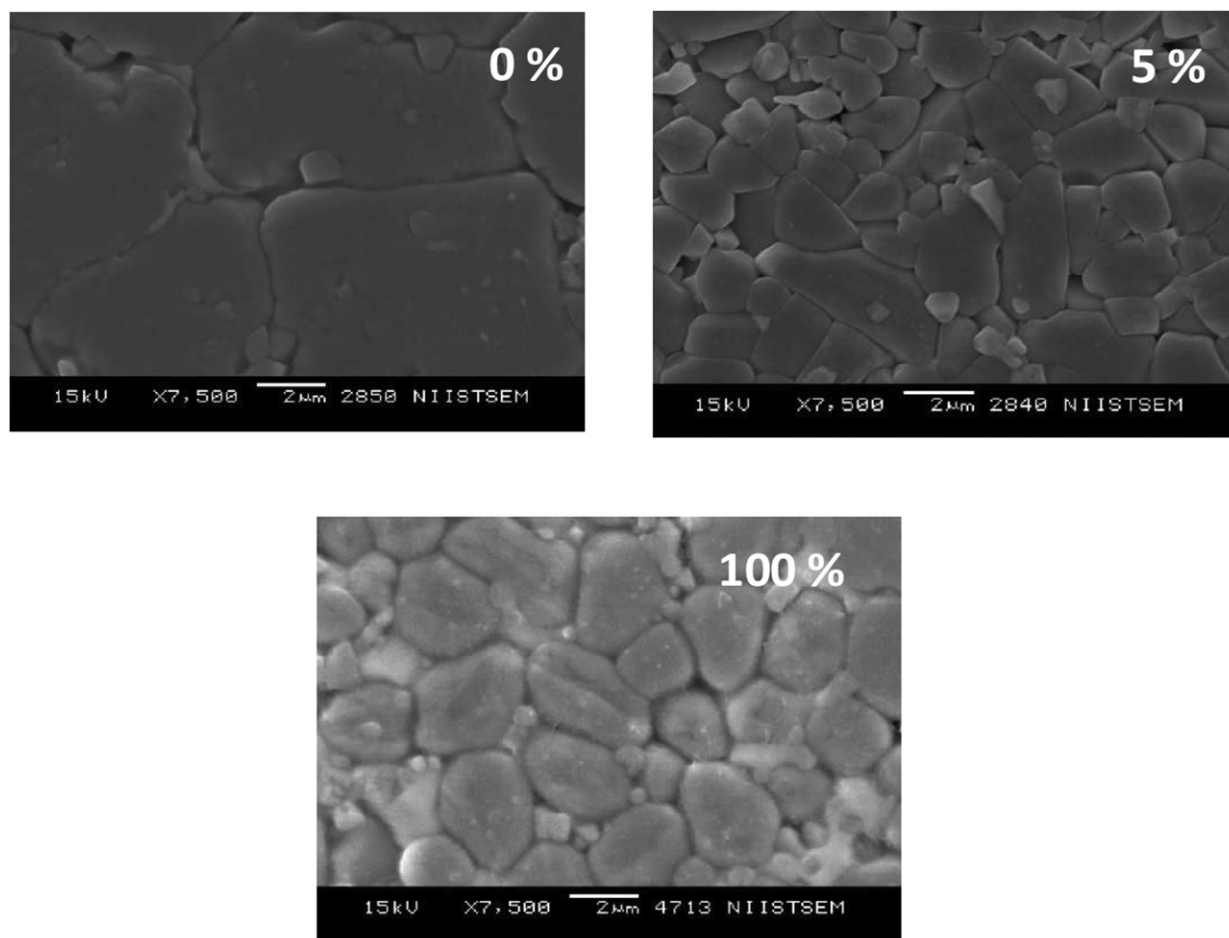


Fig. 16 SEM images of varistors containing 0%, 5% and 100% nanofiller added to commercial varistor powders. Reproduced from Anas, S., Mahesh, K.V., Jobin, V., Prasanth P., Ananthakumar, S., 2013. Nanofillers in ZnO based materials: A ‘smart’ technique for developing miniaturized high energy field varistors. *Journal of Materials Chemistry* 1, 6455–6462.

Planetary milling and nano ZnO particles

The effect of nano ZnO particles (30, 50, 90 and 500 nm) on the microstructure and electrical properties of varistors was studied by [Chen et al. \(2021\)](#). The size of the mixed oxide additives (Bi, Sb, Co, Cr, Mn, Y and Al) was kept constant, and much larger than the ZnO particles, with an average particle size of $1.0 \pm 0.5 \mu\text{m}$, typically used in industry ([Alamdari et al., 2000](#); [Yan et al., 2020](#); [Kelleher, 2003](#)). Planetary milling was used to mix the dopant oxides with the different nanosized ZnO powders. The size of the nano ZnO particles had a slight effect on the average size of the ZnO grains but had a significant effect on the electrical properties. All varistors showed very high breakdown voltages, nonlinearity coefficients and low leakage currents. The optimum ZnO particle size was 90 nm. It showed the highest breakdown voltage, 1015 V mm^{-1} , nonlinearity coefficient, 38, lowest leakage current, 2.45, and highest density, 99%, when sintered at 1100°C , [Table 14](#).

Cryo-milling of ZnO

Cryogenic milling renders the material brittle by cooling in liquid nitrogen. ZnO nanorods particles were milled by [Genç \(2017\)](#) for 5 min in a cryo-mill, Spex™ 6870 Freezer/Mill, from 59.1 to 33.4 nm. The enhanced density, 95.4%, observed for the cryo-milled powders when sintered at 1100°C compared to those which were not milled 86.3%, was attributed to the change in strain observed in the particles.

Prior preparation of constituent phases method & planetary ball milling

This method is based on sintered ZnO varistors consisting of three phases: ZnO, spinel, and intergranular bismuth. Each phase was prepared separately prior to sintering. ([Branković et al., 2000, 2007](#); [Žunić et al., 2007](#); [Bernik et al., 2008](#)). The composition of the doped three phases is summarized in [Table 13](#). Only densification and grain growth occurred during sintering ([Branković et al., 2007](#)). A schematic presentation of the method used to prepare the ZnO varistor ceramics is shown in [Fig. 13](#) ([Branković et al., 2000](#)). A milling stage (homogenization) was used to prepare each of the three phases as well as to mix them together using a

Table 15 The effect of chemical method on the powder, electrical and microstructural properties of ZnO-Bi₂O₃ varistors

Method Author (year)	ZnO varistor composition or dopants	Particle size (nm)	Sintered temperature (°C)	T.D. (%)	Average grain size, (μm)	E_b V mm^{-1}	α	J_L (μA cm^{-2})
Coprecipitation methods								
Hishita <i>et al.</i> (1989) (Amine)	Batch 1: Coprecipitate containing ZnO, Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ and Cr ₂ O ₃	200	1150		4.3	516	50	
			1200		5.2	339	52	
	Batch 2: ZnO precipitate ball milled with coprecipitate of (Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ and Cr ₂ O ₃)	–	1200			270	42	
Haile <i>et al.</i> (1989) (Aqueous)	Batch 3: Ball mill ZnO, Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ and Cr ₂ O ₃ prepared separately by precipitation.	–	1200			250	33	
	Precipitate of ZnO plus coprecipitate containing Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO ₂ and Cr ₂ O ₃	–	1200	97		210	44	
	Ball milling mixed metal oxides.	–				180	15	
Viswanath <i>et al.</i> (1995)	Precipitate of ZnO plus coprecipitate containing Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, SnO, Boron and CuO ₂ .	–	750		0.05	3000	50	
Li <i>et al.</i> (2006)	Coprecipitate of dopants (Bi ₂ O ₃ , Sb ₂ O ₃ , CoO, Cr ₂ O ₃ , MnO and SiO ₂) on ZnO powder.	–	1050		2–8	375	50	
Wang <i>et al.</i> (2008)	Conventional mixed metal oxides	–			–	325	24	
	Coprecipitate of dopants (Bi ₂ O ₃ , TiO ₂ , CoO, MnO, NiO, and SnO ₂) on ZnO powder.	–	1200		25.4	87.5	32.5	
	Conventional mixed metal oxides		1200		34.1	68.9	24.1	
Beynet <i>et al.</i> (2015)	Coprecipitation of doped (Bi, Sb, Co, Mn and Ni) Zn oxalate precursor.	20–700	SPS 870/1/100 +	98	2–3	1182	28	
	Conventional mixed metal oxides	300–1000	anneal 750°C/10 h	98	1–2	880	27	
Sol-gel methods								
Hohenberger and Tomandl (1992)	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₂ O ₃ , MnO ₂ , Cr ₂ O ₃ , B ₂ O ₃ , Al ₂ O ₃ .	1000	1100	–	4.2	375	57	0.9
Sinha and Sharma (1997) (Citrate)	Commercial varistor	–	–	–	4.3	225	47	7–70
	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₂ O ₃ , MnO ₂ , Cr ₂ O ₃ .	37	1150	98	–	515	35	11
	Coprecipitation same but with urea (Sonder <i>et al.</i> , 1985)	70	1150	94	–	280	21	35
Puyané <i>et al.</i> (1998).	Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₂ O ₃ , MnO, NiO.	< 8800	–	–	–	259	23	–
Banerjee <i>et al.</i> (2001) (Sol-Gel coating of ZnO powder)	Conventional mixed oxides	–	–	–	–	215	25	–
	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO ₂ , Cr ₂ O ₃ , NiO, Al ₂ O ₃ .	–	1080		< 10	330	51	
	Conventional mixed oxides	–	1080		< 10	301	30	
Pillai <i>et al.</i> (2003) (Core shell coating of nano ZnO particles with sol-gel dopants)	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO, NiO, Cr ₂ O ₃ , Al ₂ O ₃ .	34	1050	97	< 3	850	33	
	Sol-gel ZnO nano particles mixed with metal oxide dopants.	–		92	–	683	30	
	Commercial varistor, MLV	–	–	96	< 10	507	48	
Pillai <i>et al.</i> (2004a) (Nano-array ZnO by sol-gel and metal oxide dopants)	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO, NiO, Cr ₂ O ₃ , Al ₂ O ₃ .	–	1050	96	–	786	34	
Pillai <i>et al.</i> (2008) (Mixed Precursor Method, MPR, Disks)	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO, NiO, Cr ₂ O ₃ , Al ₂ O ₃ .	–	1050	99.6		859	33	
	Commercial varistor, MLV	–	–	96.4	–	507	28	
	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, Cr ₂ O ₃ .	–	1150		97	323	16	8
Anas <i>et al.</i> (2010) (Non-hydrolytic sol-gel)			1050		91	493	36	2–4
			950		89	557	34	< 2
Metallorganic polymeric methods								
Durán <i>et al.</i> (2001) (Metallorganic polymeric Zn and dopants)	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO.	28	1200	100	9	230	26	
		28	940	98	0.5	1587	> 70	
	Conventional mixed oxide route	1500	1200	94	9	200	< 16	

(Continued)

Table 15 Continued

Method Author (year)	ZnO varistor composition or dopants	Particle size (nm)	Sintered temperature (°C)	T.D. (%)	Average grain size, (μm)	E_b V mm^{-1}	α	J_L (μA cm^{-2})
Microemulsion methods								
Hingorani <i>et al.</i> (1993)	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO, Cr ₂ O ₃ (ZnO by micro-emulsion and dopants by precipitation)	14	1200	–	2.5	450	83	
	(ZnO metal oxide and dopants by precipitation)	20	1200	–	5	290	29	
Singhal <i>et al.</i> (1997) (ZnO by microemulsion and dopant oxides by milling)	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO, Cr ₂ O ₃	5–8	1200	–	13.9	105	76	
		10–13	1200	–	11.45	150	122	
Combustion methods								
Hwang and Wu (2004) (glycerin)	–	–	1050	92	–	205	42	1.15
Hembram <i>et al.</i> (2011) (sucrose)	ZnO, Sb ₂ O ₃ , Bi ₂ O ₃ , Co ₃ O ₄ , MnO ₂ and Cr ₂ O ₃	15–45	925	97	2.8	887	112	4.98
Liu <i>et al.</i> (2015) (xanthan gum)	ZnO, Bi ₂ O ₃ , Co ₃ O ₄	–	1150	95.5	4–10	310	27	–
Spray pyrolysis methods								
Milošević <i>et al.</i> (1993) (Spray pyrolysis of solution)	ZnO, Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO, Cr ₂ O ₃ , NiO	3000	1200	–	–	760	30	
Lin <i>et al.</i> (1999) (Cocprecipitation & Spray plasma pyrolysis)	ZnO, Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO, Y ₂ O ₃	10–50	1050	–	0.7	500	54	
		10–50	1200	–	–	–	20	
Pillai <i>et al.</i> (2004a) (Solid state pyrolysis nano ZnO)	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO, NiO, Cr ₂ O ₃ , Al ₂ O ₃	ZnO 61 (TEM)	1050	91	2	656		
Vuković <i>et al.</i> (2015) (Solid state pyrolytic reaction of ZnO & SPRT Bi ₂ O ₃ & precipitation of Sb ₂ O ₃)	Sb ₂ O ₃ , Bi ₂ O ₃ , CoO, MnO.	13	770	97	0.73	3200	71	7.7

T.D.: Percent of theoretical density, I_L : leakage current density at 75% of the breakdown voltage, E_b : breakdown voltage at 1 mA.cm⁻², α : coefficient of nonlinearity (1–10 mA cm⁻²), J_L ($\mu\text{A cm}^{-2}$): Leakage current is measured at the voltage of 0.8 K_c, D: average ZnO grain size, S.D.: percent standard deviation in grain size. L.D.: Laser diffraction, Z.S.: ZetaSizer, XRD: X-ray diffraction, T.E.M.: Transition electron microscope, SPS: Spark Plasma Sintering.

Note: Reproduced from Pillai, S.C., Kelly, J.M., McCormack, D.E., Ramesh, R., 2013. Advances in the synthesis of ZnO nanomaterials for varistor devices. Journal of Materials Chemistry C 20, 3268–3281.

planetary mill. Both the doped γ -Bi₂O₃ and spinel phases were prepared from individual metal oxide powders, mixed, milled using planetary ball milling and calcined. The doped ZnO phase was prepared by suspending the ZnO powder in an aqueous solution containing Mn(CH₃COO)₂ and Co(NO₃)₂, followed by drying, calcining and milling.

Prior preparation of the three constituent phases showed higher densities (95%) and smaller ZnO grains (5.92 μm) compared to those prepared by the mixed metal oxide route (92%, 6.3 μm). They also showed higher breakdown voltages, 437 V mm⁻¹, nonlinearity coefficient, 50, and lower leakage current, 4.5 A m⁻², compared to those prepared by the mixed metal oxide route, 268 V mm⁻¹, 41, and 19.2 A m⁻² respectively, Table 14 (Žunić *et al.*, 2007). Higher intensity milling (planetary, 2 h, 340 rpm) increased the sintered density, the breakdown voltage, and nonlinearity coefficients even further, as well as reducing the leakage current and grain size, Table 14. With a density of 98%, V_b of 895 V mm⁻¹, α of 53 and I_L of 2.5 A m⁻², these values are higher than those obtained by many of the chemical methods investigated, Table 11. High density is an important factor for high energy absorption capability.

The microstructures, Fig. 14, showed that the density increased, the average and distribution in size of the ZnO grains decreased, homogeneity of the secondary phases increased, and the concentration of the inversion boundaries (IBs) increased with both prior preparation of the three constituent phases and with increase in the intensity of milling.

Nanofilled powders

Anas *et al.* (2013) prepared a varistor powder using a reflux chemical method, containing Zn, Bi, Sb, Co and Cr, with nanorod morphology, and mixed it using a mechanical wet mixing technique with different concentrations with a commercial mixed oxide powder which had been spray dried, Figs. 15 and 16. The highest breakdown voltage, 875 V mm⁻¹, and nonlinear coefficient, 31, was obtained when 5 wt% nanofiller powder was used with the commercial powder, Table 14.

Chemical methods

Chemical methods are generally used to prepare powders from synthetic materials or from naturally occurring raw materials that have undergone a considerable amount of refinement. The purpose of the chemical methods developed for ZnO varistor powders has been to mix the metal oxide ingredients on an atomic or molecular scale without the introduction of impurities. They offer

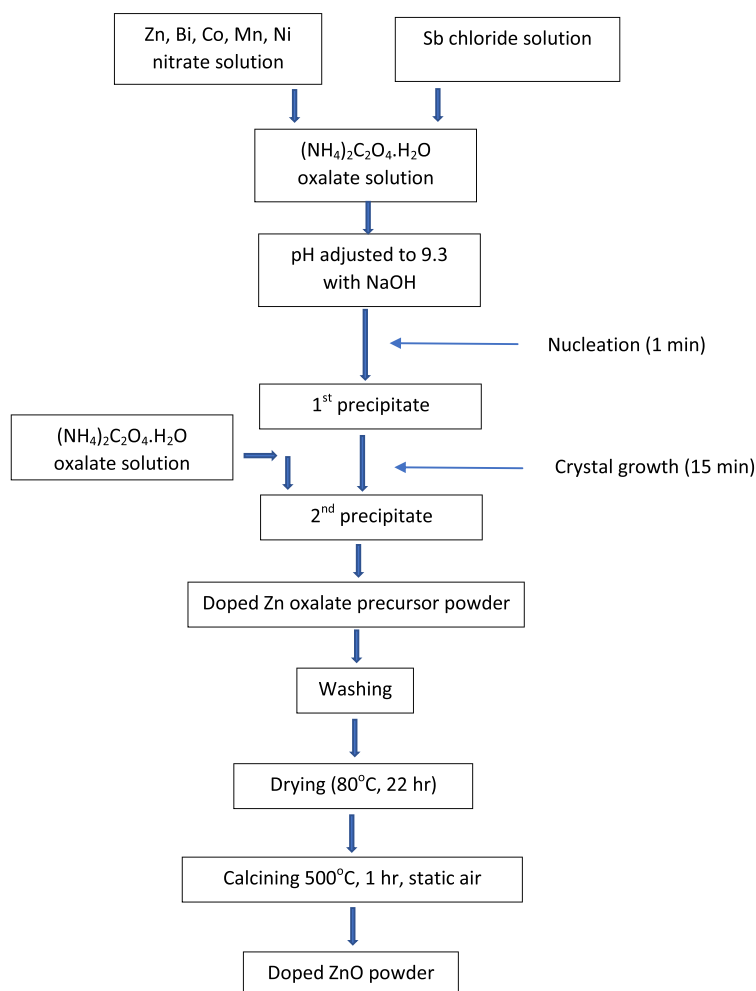


Fig. 17 Schematic representation of the coprecipitation method to form doped ZnO powder. Adapted from Beynet, Y., Izoulet, A., Guillemet-Fritsch, S., *et al.*, 2015. ZnO-based varistors prepared by spark plasma sintering. *Journal of the European Ceramic Society* 35, 199–1208.

high chemical purity and homogeneity. However, some of the methods categorised as chemical include a mechanical milling method as part of the process. It is usually necessary for the breakdown of agglomerates and to produce the desired physical characteristics of the powder such as particle size and particle size distribution. These methods, based mainly on wet chemical techniques, are: co-precipitation (Hishita *et al.*, 1989; Haile *et al.*, 1989; Viswanath *et al.*, 1995; Li *et al.*, 2006; Wang *et al.*, 2008; Beynet *et al.*, 2015), sol-gel processing of both colloids and metal-organic compounds (Hohenberger and Tomandl, 1992; Sinha and Sharma, 1997; Puyan  *et al.*, 1998; Banerjee *et al.*, 2001; Pillai *et al.*, 2003; Pillai *et al.*, 2004a; Pillai *et al.*, 2008; Anas *et al.*, 2010), metallorganic polymeric methods (Dur n *et al.*, 2001), microemulsion methods ((Hingorani *et al.*, 1993; Singhal *et al.*, 1997), combustion methods (Hwang and Wu, 2004; Hembram *et al.*, 2011; Pillai *et al.*, 2013; Liu *et al.*, 2015), and spray plasma pyrolysis methods (Milo ević *et al.*, 1993; Lin *et al.*, 1999; Pillai *et al.*, 2004a; Vukovi  *et al.*, 2015), **Table 15**. An example of a powder prepared by coprecipitation is that by Beynet *et al.* in 2015. The method is schematically represented in **Fig. 17**. There are many additional stages to the process compared to the conventional mixed oxide route.

Conclusions

The mechanical methods explored to date for preparing powders have shown a strong influence on the characteristics of the powders and consequently on the microstructural and electrical characteristics of the varistors. Increased homogeneity of the dopants in the powders because of increasing milling duration and intensity has had a positive effect on the homogeneity of the secondary phases and ZnO grain size distribution of the sintered varistors. The corresponding electrical characteristics in the low current region also improved. It has been shown that varistors with high densities, greater than 98% of theoretical density, high breakdown voltages of 565, 895 and 1015 V mm⁻¹, high nonlinear coefficients, 75, 53 and 37.9, and low leakage currents, 0.45, 2.5 and 2.45 µA cm⁻², are possible when sintered at temperatures ranging from 1075° to 1200°C (Zhu *et al.*, 2012;  uni 

et al., 2007; Chen *et al.*, 2021). Planetary milling was used to prepare these powders and the electrical characteristics are comparable with many of the varistors prepared from chemical methods.

Several researchers using chemical methods for making varistor powders showed that it is possible to make varistors with microstructures with high density, very homogeneous and very small ZnO grains. Pillai *et al.* (2008) and Durán *et al.* (2001) succeeded in making varistors with densities of 99.9% and 98% of theoretical density, breakdown voltages of 859 and, 1587 V mm⁻¹ and nonlinear coefficients of 70 from powders made using a mixed precursor method and metallorganic polymeric method, and sintering the disks at 1050 and 940°C, respectively. Hembram *et al.* (2011) and Vuković *et al.* (2015) reported extraordinary electrical characteristics for varistors made using a combustion method, with sucrose, and a solid-state pyrolytic reaction, while obtaining 97% of theoretical density at very low sintering temperatures, 925 and 770°C, respectively. They showed that breakdown voltages of 887 and 3200 V mm⁻¹, high nonlinear coefficients, 112 and 71, and low leakage currents, 4.98 and 7.7 µA cm⁻², are possible from ZnO varistors prepared powders made with these methods.

Future Directions

The improved microstructural and electrical characteristics are promising for the making smaller ZnO varistors which would require less material. However, the extra processing stages required, and the associated costs, and reproducibility needs to be evaluated.

There is no doubt that the powder preparation method, in addition to the composition and sintering, plays a very important role in the microstructure and electrical properties of ZnO varistors. Analysis of the I-V characteristics of the individual grains was mainly carried out on ZnO varistors prepared from the conventional mixed metal oxide method using micron size metal oxide particles. It would be interesting to compare the I-V characteristics of the individual grain boundaries of the varistors with improved microstructural and electrical characteristics made using these mechanical and chemical powder preparation methods.

The lower current characteristics have been evaluated for most methods investigated and developed for ZnO varistors. The high current characteristics, low current stability and energy capability are also very important and would be valuable when deciding to choose a powder preparation method for implementation on an industrial scale. Other factors that are important when deciding to implement on an industrial scale are the cost associated with the extra stages, space, materials, and chemicals, how easy is it to scale up, how easy is it to produce, repeatability within a batch and between batches, and number of suppliers.

To allow successful transfer of new methods from the laboratory to pilot line or industry more knowledge is required of the chemical and physical properties of the raw materials, indirect materials (e.g., grinding media materials, wear) and equipment used.

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Metamaterials: Engineered Materials and its Applications in High Frequency Electronics

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Abstract

Metamaterials are described as engineered periodic composites for altering electromagnetic properties of materials to obtain responses that are not observed naturally. This article bestows the sequential development of electromagnetic metamaterials with a lucid explanation of the electrodynamics of these engineered materials that are subwavelength in dimension. Periodic arrangement of the subwavelength structures has a collective behavior as a material. The physical implementation of metamaterials is revisited. The computation complexity of detailed metamaterial macrostructures has been discussed, and hence the advantage of homogeneous modeling of metamaterials is explained. Further, metamaterial-inspired geometries and their varied application in microwave paradigm are discussed vividly.

Key Points

- Metamaterials are described as engineered periodic composites for altering electromagnetic properties of materials to obtain responses that are not observed naturally.
- This article bestows the sequential development of electromagnetic metamaterials with a lucid explanation of the electrodynamics of these engineered materials that are subwavelength in dimension.
- Periodic arrangement of the subwavelength structures has a collective behavior as a material.
- The physical implementation of metamaterials is revisited. The computation complexity of detailed metamaterial macrostructures has been discussed, and hence the advantage of homogeneous modeling of metamaterials is explained.
- Further, metamaterial-inspired geometries and their varied application in microwave paradigm are discussed vividly.

Introduction

Although the presence of metamaterial was first proposed in 1967 by Veselago (Translated in english in 1968 (Veselago, 1968)), it was after 1996 that scientist and engineers first began to realize engineered material systems that could generate a left handed medium (LHM). The preexistent work before the contribution by John Pendry of Imperial College in 1996, investigations of the properties of a LHM was theoretical; which was concentrated in exploring the effects of their innovative properties depending on the solutions of Maxwell equations. Pendry's work (Pendry *et al.*, 1996) started with creating metamaterials (MTM) that had unique electromagnetic properties. First, a pseudo material with a negative permeability with an array of conducting wires was realized that had properly chosen spacing and radii. Metamaterials as LHMs have subwavelength features artificially tuned to exhibit in some cases negative refractive index over a frequency range. Another name given to these materials is double negative (DNG) materials. A pictorial representation of various kinds of materials depending on the permittivity and permeability values is provided in Fig. 1. In 1999 Pendry (Pendry *et al.*, 1999) contemplated that an array of split ring resonators (SRR) would have a region of negative permeability over a restricted band of frequencies, analogous to a magnetic material.

Though Pendry's work had given the substratum, it was Smith *et al.* at the University of California, San Diego (UCSD) who constructed a meta-material that includes an array of wires and SRRs (Smith and Kroll, 2000). Metamaterials can be visualized as a kind of organized composites that shows unique traits not observed naturally. The initial study included wave propagation through metamaterial region (Mukherjee *et al.*, 2012) and use of the unit cells to design and tune antenna characteristics. The later ones being known as metamaterial-inspired antenna.

The fundamental units can be periodically arranged to make it appear as a homogeneous metamaterial volumetric region or a surface, a two dimensional extension of the volumetric concept of these artificially engineered materials. These periodically placed structures can provide electrical characteristics like bending of electromagnetic waves, absorption of electromagnetic energy, and altering phase velocity of electromagnetic wave traveling through the material (Dong and Itoh, 2012a,b). These phenomena have been realized from RF to the optical domain. The microwave regime being attractively explored due to more penetrating power of this frequency region and providing mechanism for design of compact antenna, multiband antenna, meta-surface as a facilitator for obtaining circularly polarized radiations and gain enhancement (Jash *et al.*, 2019; Feresidis *et al.*, 2005). Perhaps, the periodic array profile consisting of sub-wavelength structures was attractive due to its compact nature as the size was an obvious reason for low gain of an antenna using such small-sized resonators.

It may be observed that the tailored electrically small resonators that comprise the seemingly homogeneous block provide an effective medium in which the electromagnetic wave propagation can be altered to bring forth lensing action (Dong and Itoh, 2012a,b; Mosallaei and Sarabandi, 2004). This can result in gain enhancement with a focusing mechanism. Artificial magnetic

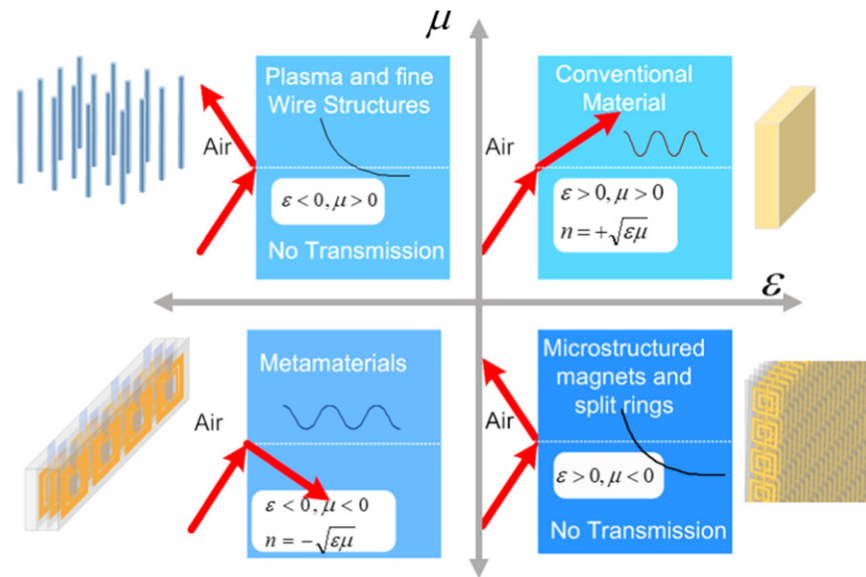


Fig. 1 Classification of materials based on the value of permittivity and permeability.

conductors (AMC) are a variant in the 2D metamaterial regime. These provide a method to minimize surface wave in microstrip antenna as well as provide enhancement of gain. There are applications where MTM can be used to make the incoming electromagnetic wave not reflect to the source or get scattered in other directions (Alitalo and Tretyakov, 2009; Schurig *et al.*, 2006; Alitalo *et al.*, 2008). This is known as cloaking.

It is well known that a resonant element can be put to an application as a radiator as well as a component to receive electromagnetic energy. Therefore, in addition to the metamaterial and meta-surfaces, the building blocks of these homogeneous structures also found numerous applications where the sub-wavelength resonators were used to modify the performance of an antenna (Goswami *et al.*, 2018). Sub-wavelength structures have also found application in bringing about stopband characteristics in wideband antenna systems (Gorai and Ghatak, 2019).

Another interesting observation can be made regarding the sub-wavelength structures that form the basis of a homogeneous MTM. This is the quality factor of the electrically small resonators, which is suitably high to obtain sharp resonance. It conveys the suitability of these resonators in telemetric sensing applications that are based on frequency variation. Higher resonance frequency variations enhance the sensitivity of these resonators to be used for high sensitivity sensing (Melik *et al.*, 2009). Such sensors using an array of SRR have been used for monitoring the healing process in long bone fractures (Melik *et al.*, 2009, 2010). Sensors using SRR have been used to detect angular displacement and velocity using the amplitude modulation approach (Contreras *et al.*, 2017). Displacement and alignment sensors using SRR have also been reported (Horestani *et al.*, 2014) that employ the concept of change in the depth of the notch at a given frequency. In (Mandel *et al.*, 2011), frequency variation is measured to determine the amount of bending or strain by incorporating mushroom micro-resonators. Differential sensing using a frequency split approach has been used to determine the dielectric permittivity of a material (Ebrahimi *et al.*, 2018).

An electromagnetic absorber neither transmits nor reflects incident radiation but absorbs the power of the incident wave at their resonance (Liu *et al.*, 2010; Wu *et al.*, 2011). The technique of controlling the operation frequency by tuning the constituting unit cell metamaterial parameters can be applied at higher frequencies as well until the metal skin depth and unit cell dimension become comparable (Cheng *et al.*, 2012). For regions showing a very low absorption rate, the reflection rate is high there. Thus through proper tuning of the metamaterial parameters, we can either construct a metamaterial absorber or a metamaterial reflector.

To analyze the absorption properties, various theories have been propounded like resonant absorption theory (Chen *et al.*, 2010), interference theory (Wanghuang *et al.*, 2013; Pang *et al.*, 2011), equivalent circuit theory (Pang *et al.*, 2013; Bhattacharyya *et al.*, 2014), impedance matching theory (Cheng and Gong, 2013), reflection theory etc. Among all the theories, excepting reflection theory, each one of them is having limitations. In resonant absorption theory, the absorption is contributed by electric and magnetic plasmon resonance and it fails to explain the working of intrinsic absorption mechanism. In addition to resonance, interference theory gives the relationship with the half wavelength phase difference between two reflection waves and magnitude of S-parameters but it cannot explain the dependence of absorptivity on spacer thickness and absorption frequency. Though the equivalent circuit method can analytically explain the relationships among spacer thickness, permittivity of the dielectric substrate, and reflection characteristics, but is only suitable for normal incidence and not oblique incidence. Impedance matching theory is the most widely used theory and is inherent in all the absorption mechanisms. Reflection theory is the most acceptable one and it gives the relation between spacer thickness, absorption frequency, effective dielectric parameters, loss tangent of dielectric and incident angles to affect absorption (Xiong *et al.*, 2015).

Fundamentals of Metamaterial

For a material the response to the applied electromagnetic wave can be determined by two electromagnetic parameters, magnetic permeability μ and electric permittivity ϵ . Referring to Fig. 1, the double positive materials occur in the form of well known dielectrics. Single negative media with negative permittivity can be observed in plasma and metals at optical frequencies. Ferrites at microwave frequencies exhibit negative permeability resulting in a variant of single negative medium. What is interesting is the occurrence of double negative (DNG) behavior in composites that are not available in nature. These can be synthesized at a given frequency with the realization of sub-wavelength structures that are arranged periodically (as a lattice structure) with a spacing such that it appears as a homogeneous media for the impinged electromagnetic wave. The article aims to delve in to the realization of such fundamental structures that can be used to form such DNG medium. The overall effect of the interaction of the electromagnetic wave with the DNG medium can be analyzed by considering the refractive index, which is $n = \sqrt{\epsilon\mu}$. With both the permeability and permittivity being negative, the refractive index of the DNG medium can be obtained as given in (1)

$$n = \sqrt{(-\mu_r)(-\epsilon_r)} = (\mu_r(e^{-j\pi})\epsilon_r(e^{-j\pi}))^{1/2} = \mu_r(e^{-j\pi/2})\epsilon_r(e^{-j\pi/2}) = \sqrt{\mu_r\epsilon_r}e^{-j\pi} < 0. \quad (1)$$

From eq. (1), it can be inferred that it is the phase of the electromagnetic parameters that contributes to negative values of refractive index.

Metamaterial with such unusual behavior can render some typical physical phenomena such as backward-wave propagation, negative refraction, and "amplification" of evanescent waves. The Maxwell's curl equations denoting the Faraday's law and Ampere's law are given in (2) and (3), respectively.

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (2)$$

$$\nabla \times \vec{H} = \frac{\partial \vec{D}}{\partial t} \quad (3)$$

where $\vec{E}$ is the electric field intensity, $\vec{B}$ is the magnetic flux density, $\vec{H}$ is the magnetic field intensity and $\vec{D}$ is the electric flux density.

For uniform plane waves one can obtain

$$\vec{k} \times \vec{E} = \mu\omega\vec{H} \quad (4)$$

$$\vec{k} \times \vec{H} = -\epsilon\omega\vec{E} \quad (5)$$

where $\vec{k}$ is the wave vector.

From eqs. (1) and (2), it can be seen that vectors $\vec{E}$, $\vec{H}$, and $\vec{k}$ form a right handed triplet of vectors for positive ϵ and μ , but left handed triple for negative ϵ and μ . This is illustrated in Fig. 2(a) and (b). This gives the idea of left handed waves. Further, the Pointing vector is given as (6).

$$\vec{S} = \vec{E} \times \vec{H} \quad (6)$$

Pointing vector always forms a right-handed triple of vectors together with the vectors $\vec{E}$ and $\vec{H}$.

The phase velocity v_p of the wave and the direction of the wave vector $\vec{k}$ has same direction whereas the direction of the group velocity v_g has the same direction as the $\vec{S}$ vector. Thus it can be inferred that the phase and group velocities are anti-parallel when

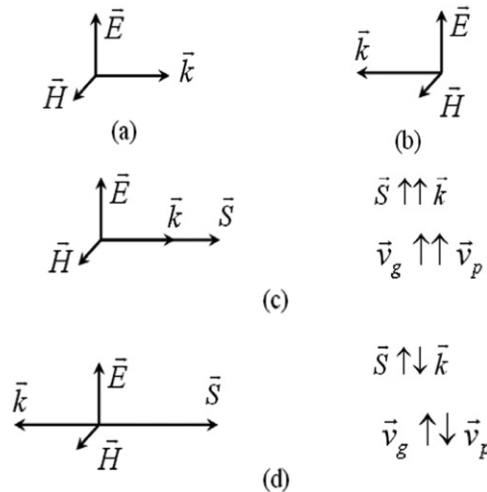


Fig. 2 Representation of Pointing vector and wave vector.

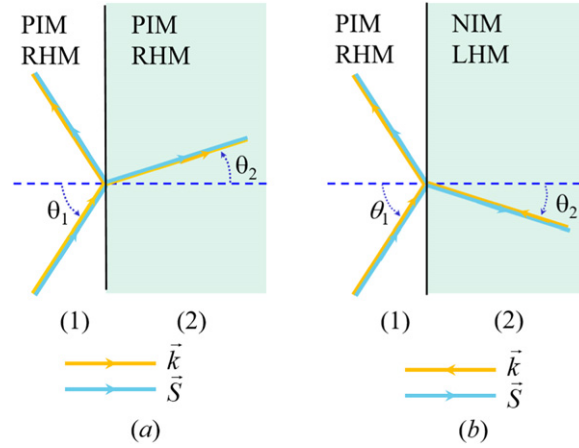


Fig. 3 Illustration of negative Snell's law in left handed materials.

ϵ and μ are negative simultaneously. In such case the wave vector and the Poynting vector are also anti-parallel. It is shown in Fig. 2(c) and (d), respectively.

As metamaterial show, anti-parallel phase and group velocities, Snell's law gets modified to give rise to negative refraction as shown in Fig. 3. This surprising propagation of the ray is a repercussion of the opposite direction of v_p and v_g and of the tangential components of the wave vector on the interface between two media being continuous. The phenomenon of anti-parallel phase and group velocities in metamaterials can be interpreted as if the electromagnetic energy travels away from the source, wave fronts travel backward toward the source in a LHM. This effect not only manifests itself as modification of Snell's law but also reverses the Cerenkov radiation and causes negative Doppler shift.

Transmission Line Theory of Metamaterial

Distributed line theory has long been a robust analysis and design tool for components and materials at microwave frequencies. Composite right/left handed (CRLH) transmission line (TL) metamaterial structures have lead to a plethora of electromagnetic concepts and applications. By modeling a CRLH metamaterials as an equivalent TL, TL theory can be effectively utilized for analysis and design of 1-D, 2-D or even 3-D CRLH metamaterials. CRLH metamaterials will be represented by an equivalent homogeneous (continuous and invariant along the direction of propagation) CRLH transmission line to have an insight into its properties. The general CRLH TL model is shown in Fig. 4.

The propagation constant of a TL is given by.

$\gamma = \alpha + j\beta = \sqrt{Z'Y'}$, where Z' and Y' are impedance and admittance per unit length given as

$$Z'(\omega) = j\left(\omega L'_R - \frac{1}{\omega C'_L}\right) \quad (7)$$

$$Y'(\omega) = j\left(\omega C'_R - \frac{1}{\omega L'_L}\right) \quad (8)$$

The dispersion relation for a homogeneous CRLH TL is simplified as

$$\beta(\omega) = s(\omega) \sqrt{\omega^2 L'_R C'_R + \frac{1}{\omega^2 L'_L C'_L} - \left(\frac{L'_R}{L'_L} + \frac{C'_R}{C'_L}\right)} \quad (9)$$

Where $s(\omega) = \begin{cases} -1 & \text{if } \omega < \min(\omega_{se}, \omega_{sh}) \text{ LH range} \\ +1 & \text{if } \omega > \min(\omega_{se}, \omega_{sh}) \text{ RH range} \end{cases}$, and ω_{se} as well as ω_{sh} are series and shunt resonant frequencies. At frequencies where propagation constant is purely real, a stop band occurs in the frequency range where β is purely imaginary since $\gamma = \alpha$. This stopband is a unique characteristic of CRLH TL, which is not present in PRH or the PLH TL. Fig. 5(a) shows the dispersion diagram of PRH TL, these diagrams shows that group velocity and phase velocity parallel and Fig. 5(b) LRH TL where group velocity and phase velocity antiparallel, 5(c) shows the CRLH TL dispersion diagram shows that it has left hand and right hand region and stop band occurs when propagation constant γ is purely real. Fig. 5(d) reveals the dispersion diagram of a balanced CRLH TL where a seamless transition from LH to RH can be observed.

Permeability and permittivity of equivalent TL model are as given below.

$$\mu = \frac{Z'}{j\omega} = L'_R - \frac{1}{\omega^2 C'_L} \quad (10)$$

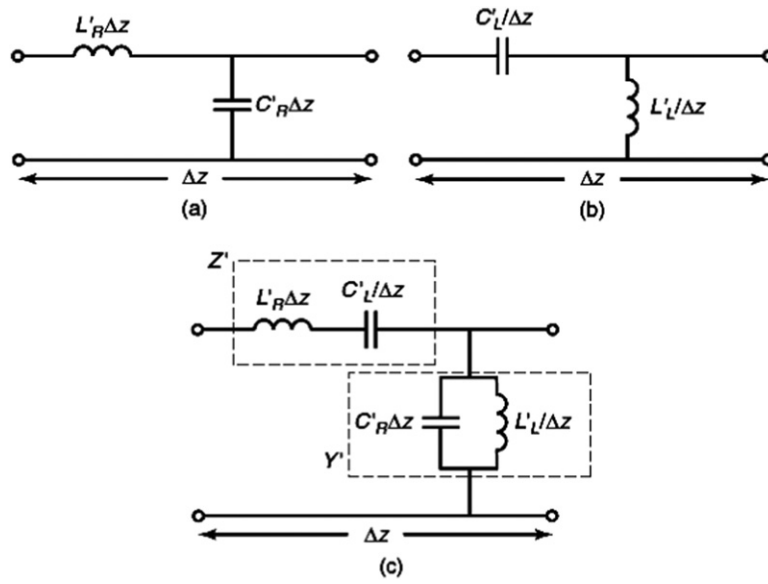


Fig. 4 Equivalent circuit model of (a) Pure RH transmission line. (b) Pure LH transmission line. (c) Pure CRLH transmission line.

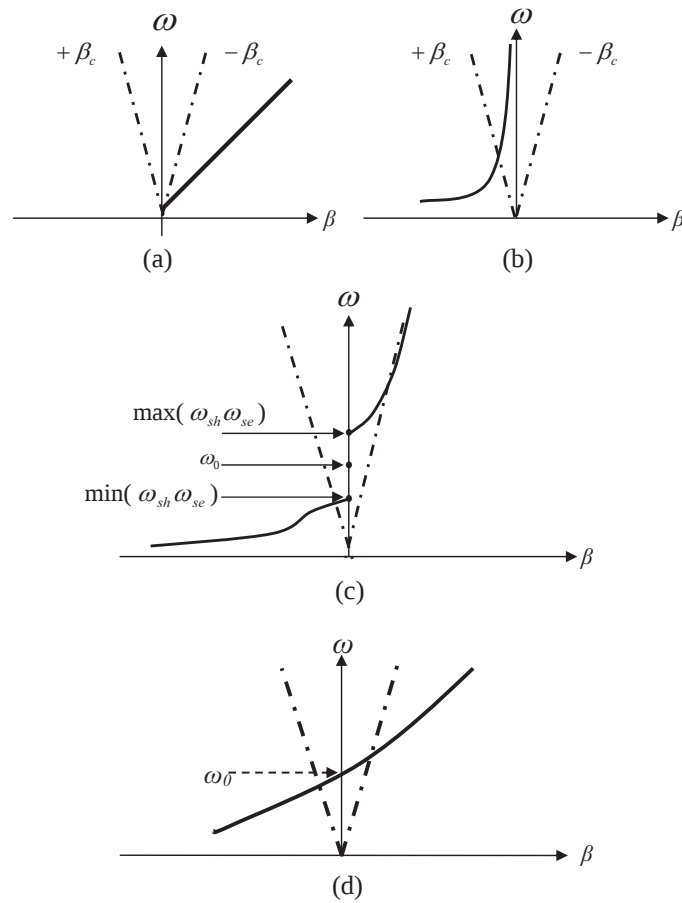


Fig. 5 Dispersion diagram for the transmission lines depicted in Fig. 4. (a) Homogeneous RH TL (b) Homogeneous LH TL (c) Homogeneous CRLH TL (unbalanced mode) and (d) Homogeneous CRLH TL (balanced mode).

$$\varepsilon = \frac{Y'}{J\omega} = C'_R - \frac{1}{\omega^2 L'_L} \quad (11)$$

In the ensuing sections, we will discuss about the realization techniques of these negative index materials and means to characterize them.

Physical Implementation of Metamaterial

Ever since the concept was first recommended by Veselago as mentioned in “Introduction” it took nearly thirty years to be practically realized at microwave frequencies. In this section, we will discuss two broad types of methods used to realize metamaterials. There are mainly two approaches to realize metamaterials. The first one is realized using wire and split ring resonator (SRR) and the other using a direct correlation with the transmission line analogy by using interdigital capacitors and stub inductors.

In 1999, Pendry *et al.* (1999) proposed a lattice of infinitely long parallel wires, and a lattice of SRRs which are relatively small when compared to the wavelength in the host medium. While the arrays of wires result in negative permittivity at certain microwave frequency bands and the array of SRR gives rise to negative permeability. An array of wire is shown in Fig. 6.

The negative permittivity is for normal propagation of waves with respect to the wires with the electric field polarized along the wires. For perfectly conducting wires the permittivity is given as (11)

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega^2} \quad (12)$$

In (11) ω_p is the analogous plasma resonance. With the periodic placement of rings along with the wires result in negative permeability. The SRR as shown in Fig. 7 consists of two concentric rings with opening oppositely directed. The capacitance between the two rings is balanced by the inductance. A magnetic field which varies with time, when applied perpendicular to the ring surface results in induction of currents which, depending on the resonant traits of the structure, produce a magnetic field that may either oppose or increase the incident field, which yields positive or negative permeability. For a double split ring resonator of circular shape in vacuum and with imperceptible thickness the effective permeability is given as

$$\mu_{eff} = 1 - \frac{\pi r^2 / a}{1 + \frac{2\sigma i}{\omega r \mu_0} - \frac{3d}{\pi^2 \mu_0 \omega \varepsilon_0 r^3}} \quad (13)$$

In (12), a is the length of the unit cell and σ is electrical conductance.

The SRR discussed in conjunction with wires constitutes a lattice of homogenous metamaterial that exhibit negative permittivity and permeability as shown in Fig. 8. The SRRs are placed exactly at the middle of the two adjacent wires such that this interaction between the wire lattice and SRR array is not quasi-static and rather dramatically influences effective permittivity.

A complementary split ring resonator (CSRR) is a negative image of an SRR in a metallic plane (Booker, 1946) as shown in Fig. 9. The CSRR is driven by time varying electric fields to obtain negative values of effective permeability.

The CSRR in conjunction with the transmission line loaded with gap capacitance exhibit negative permittivity and permeability (Gil *et al.*, 2006) as shown in Fig. 10.

Distributed component based one dimensional CRLH transmission line was reported in (Caloz and Itoh, 2004) and is shown in Fig. 11. This structure is realized on a microstrip with interdigital capacitors and stub inductors connected to the ground plane. The unit cell of the structure as shown in Fig. 12 can be modeled using Fig. 4(c).

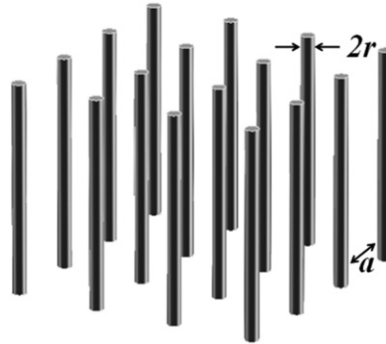


Fig. 6 Array of wire forming a negative permittivity lattice [re-illustrated from Pendry, J.B., Holden, A.J., Robbins, D.J., Stewart, W.J., 1999. Magnetism from conductors and enhanced nonlinear phenomena. IEEE Transactions on Microwave Theory and Techniques 2075–2084.].

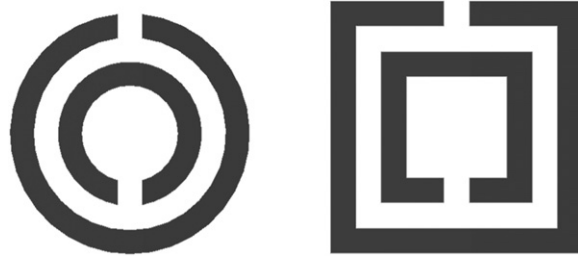


Fig. 7 Split ring resonator topology [re-illustrated from Pendry, J.B., Holden, A.J., Robbins, D.J., Stewart, W.J., 1999. Magnetism from conductors and enhanced nonlinear phenomena. IEEE Transactions on Microwave Theory and Techniques 2075–2084.].

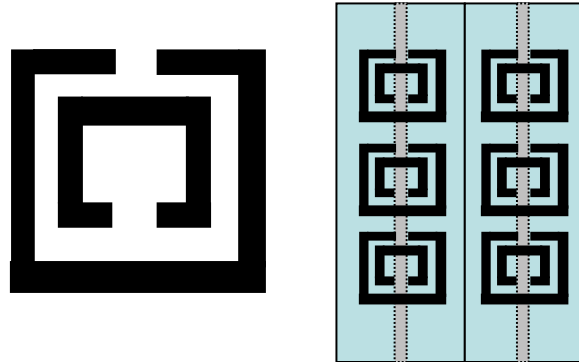


Fig. 8 SRR and wire lattice and orientations implemented in planar circuits [re-illustrated from Pendry, J.B., Holden, A.J., Robbins, D.J., Stewart, W.J., 1999. Magnetism from conductors and enhanced nonlinear phenomena. IEEE Transactions on Microwave Theory and Techniques 2075–2084.].



Fig. 9 Complementary Split ring resonator (CSRR) topology [re-illustrated from Booker, H.G., 1946. Slot aeriels and their relation to complementary wire aeriels (Babinet's principle). Journal of the Institution of Electrical Engineers 620–626.].

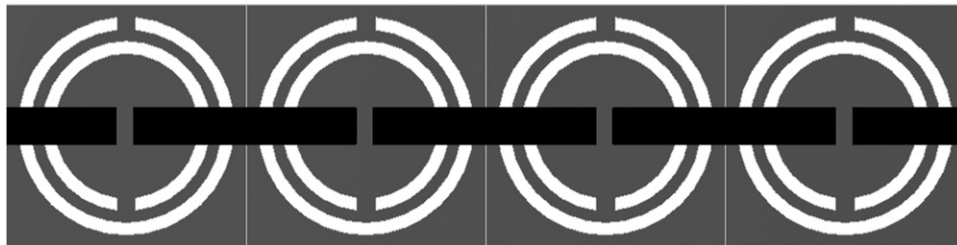


Fig. 10 CSRR and gap loaded transmission line orientations implemented in planar circuits [re-illustrated from Gil, M., Bonache, J., Gil, I., Garcia, J., Martin, F., 2006. On the transmission properties of left handed microstrip lines implemented by complementary split rings. International Journal of Numerical Modelling: Electronic Networks, Devices and Fields 87–103].

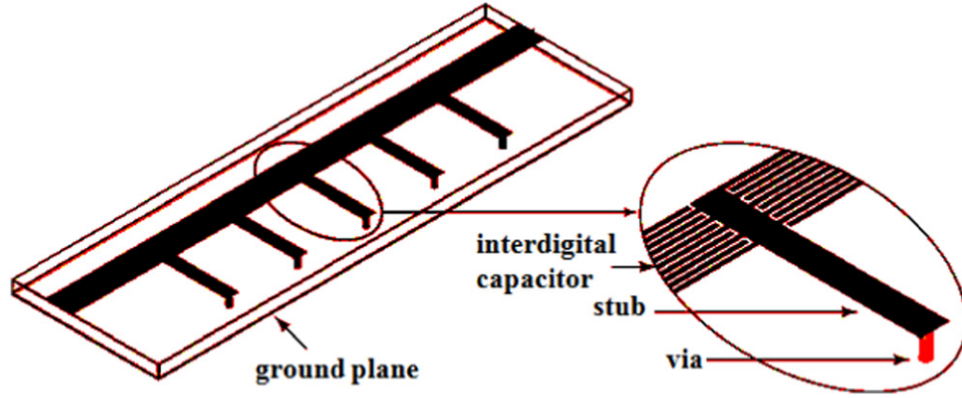


Fig. 11 Microstrip CRLH transmission line using interdigital capacitors and shorted stub resonators [re-illustrated from Caloz, C., Itoh, T., 2004. *Electromagnetic Metamaterials: Transmission Line Theory and Microwave Application*. New York: Wiley.].

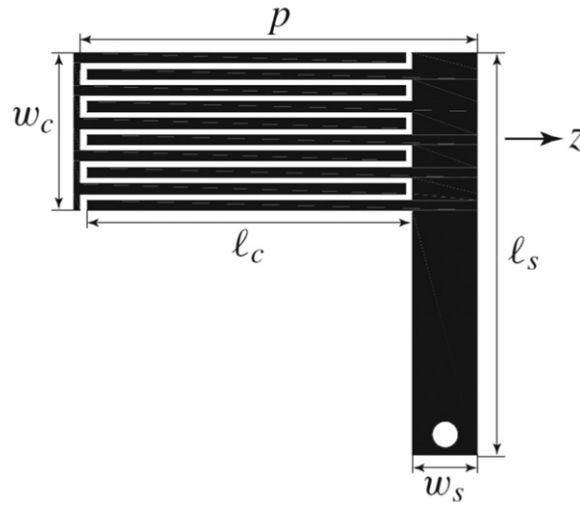


Fig. 12 Unit cell of the microstrip CRLH transmission line [re-illustrated from Caloz, C., Itoh, T., 2004. *Electromagnetic Metamaterials: Transmission Line Theory and Microwave Application*. New York: Wiley.].

Material Parameter From Extracted S Parameters

The material characteristics are determined by its permittivity, permeability and conductivity. The extraction of these values determines the nature of propagation of the material at a particular frequency.

For extraction of ϵ and μ , consider a unit cell of metamaterial is examined. Appropriate boundary conditions and excitations need to be designated to different surfaces of the three dimensional cell for simulation of the periodic metamaterial and hence extraction of the S parameters. If a wave is incident normally on the metamaterial unit cell, then the S parameters of the system can be written by using eqs. (13) and (14) which are given in (Chen *et al.*, 2004).

$$S_{11} = \frac{R_{01}(1 - e^{i2nk_0d})}{1 - R_{01}^2 e^{i2nk_0d}} \quad (14)$$

$$S_{21} = \frac{(1 - R_{01}^2) e^{i2nk_0d}}{1 - R_{01}^2 e^{i2nk_0d}} \quad (15)$$

On solving (13) and (14), gives

$$z = \pm \sqrt{\frac{(1 + S_{11})^2 - S_{21}^2}{(1 - S_{11})^2 - S_{21}^2}} \quad (16)$$

$$e^{ink_0d} = \frac{S_{21}}{1 - S_{11} \frac{z-1}{z+1}} \quad (17)$$

$$n = \frac{1}{k_0d} \left[\left\{ \left[\ln(e^{ink_0d}) \right]'' + 2m\pi \right\} - i \left[\ln(e^{ink_0d}) \right]' \right] \quad (18)$$

where $(\bullet)''$ is the representation of the complex component and $(\bullet)'$ represents the real component of the complex number; S_{11} and S_{21} are respectively the reflection and transmission coefficients, respectively; R_{01} is $\frac{z-1}{z+1}$; n is the refractive index; z implies impedance. k_0 is the wavenumber; d is the extreme length of the unit cell; m is the branch owing to the periodic nature of the sinusoidal function.

The metamaterial discussed here is represented by the cube formed by the unit cell, with appropriate excitations and boundary conditions. In this analysis, the material is assumed to be homogenous, having an effective refractive index and impedance. This is assumed for the dimension of unit cell less than one-tenth of the wavelength.

After the extraction of S parameters, the permittivity (ϵ) and permeability (μ) can be obtained using (18) and (19).

$$\epsilon = \frac{n}{z} \quad (19)$$

$$\mu = nz \quad (20)$$

However, there are various other S parameter extraction methods which are reviewed in (Arslanagic et al., 2013).

Extraction of S parameters can be done by using a full wave simulator like HFSS or CST Microwave studio. The unit cells must be repeated infinitely in the direction of lattice vectors for realization of the metamaterial. This requirement is accomplished by setting appropriate boundary conditions. As reported in (Andreone et al., 2011), a combination of perfect electric (PE) and perfect magnetic boundary conditions simulates the periodic boundary conditions by utilizing the symmetry rooted by the metamaterial. For illustration, a square shaped split ring resonator (SRR) structure reported in (Smith et al., 2005) is shown in Fig. 13 with appropriate boundary conditions. The magnitude and phase of the S parameters extracted by using CST Microwave studio are shown in Fig. 14. The permittivity, permeability, impedance, and refractive index can then be obtained by using eqs. (15) to (19). The permeability and permittivity curves obtained are depicted in Fig. 15(a) and Fig. 15(b) respectively. Similarly, Fig. 16(a) and Fig. 16(b) show the impedance and refractive index respectively.

Homogeneous Modeling of Metamaterial Media

Typically double negative metamaterials are realized by periodic arrangements of subwavelength SRRs (μ negative) and thin wires (ϵ negative). The design of homogeneous metamaterial samples require a large array of these subwavelength structures. For 3-D full wave simulation, the mesh of the structures should be very fine for proper numerical computation otherwise a continuous metamaterial sample may not be modeled properly (Lubkowski et al., 2009). This rigorous simulation requires enormous computational cost. A solution to this problem is a comparable representation of the metamaterial as a homogeneous cell characterized with predefined parameterized dispersive Drude (electric permittivity) and Lorentz (magnetic permeability) models

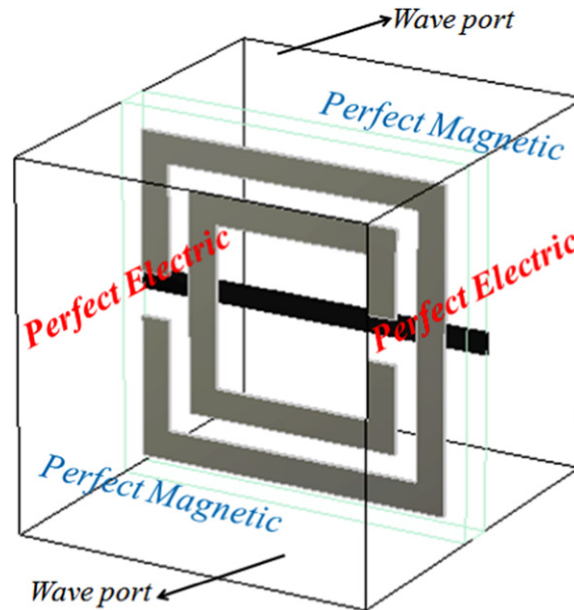


Fig. 13 The unit element with perfect electric and perfect magnetic boundary.

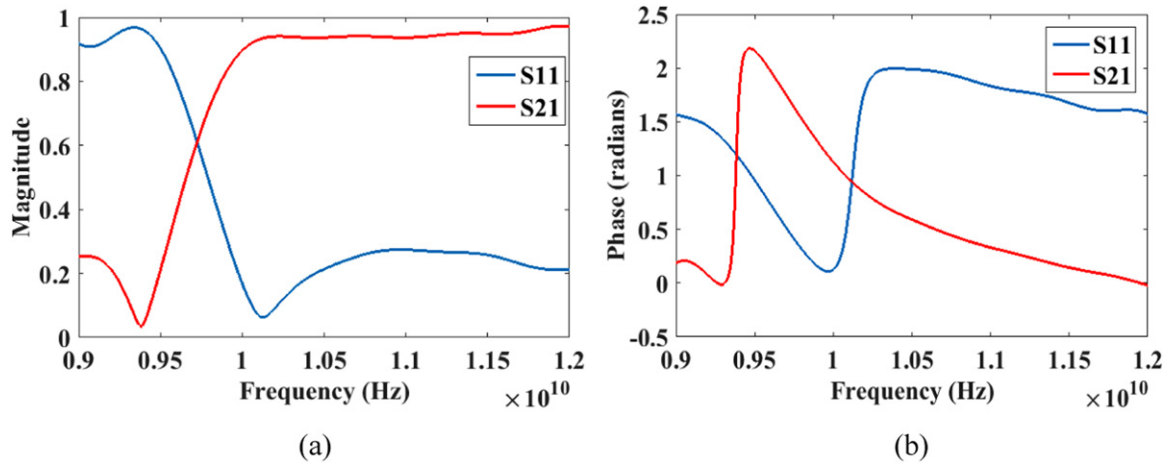


Fig. 14 (a) Magnitude of S parameter (b) Phase of S parameter.

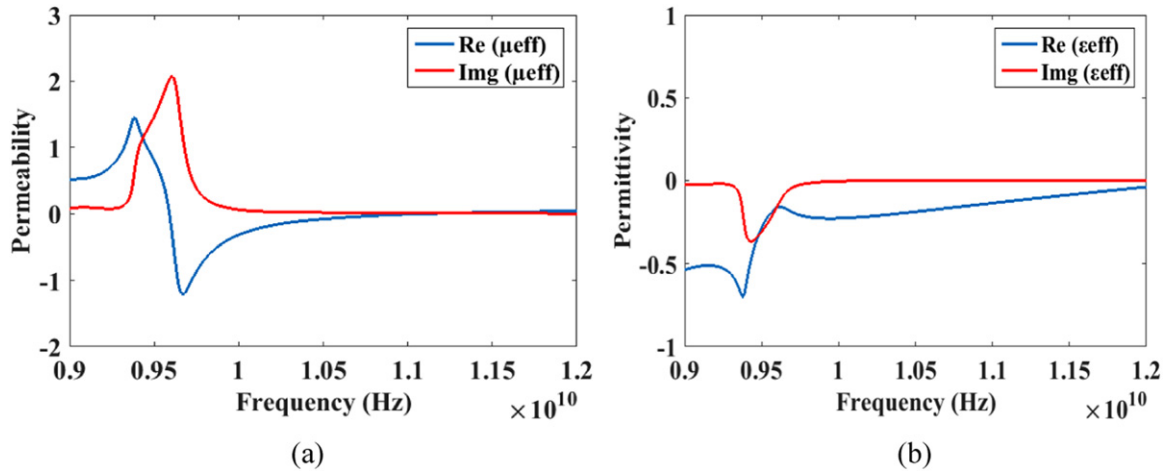


Fig. 15 (a) Permeability and (b) Permittivity variation with frequency.

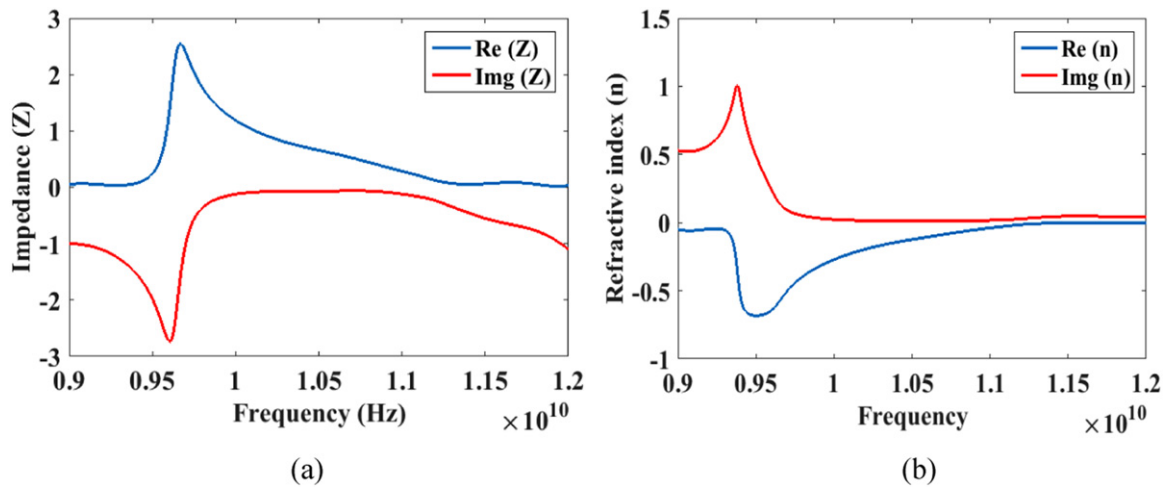


Fig. 16 (a) Impedance and (b) Refractive index variation with frequency.

(Lubkowski *et al.*, 2009). Drude/Lorentz models of the effective permittivity (ϵ_{eff}) and permeability (μ_{eff}) of the homogeneous medium are given as:

$$\epsilon_{\text{eff}}(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega - i\nu_c)} \quad (21)$$

$$\mu_{\text{eff}}(\omega) = \mu_{\infty} + \frac{(\mu_s - \mu_{\infty})\omega_0^2}{\omega_0^2 + i\omega\delta - \omega^2} \quad (22)$$

In the above equations, ϵ is the relative permittivity at the high frequency limit of the model, ω_p is the plasma angular frequency, ν_c is the collision frequency, μ_s is the static permeability, μ is the relative magnetic permeability at the high frequency limit of the model, ω_0 is the resonant angular frequency, δ is the damping frequency. An optimization algorithm can be used to search for the values of ϵ_{eff} and μ_{eff} subparameters (namely: ϵ , ω_p , ν_c , μ_s , μ , ω_0 , δ) providing the best fit between the scattering parameters of the homogenized structure and the reference structure obtained with a detailed simulation.

In (Ghatak *et al.*, 2012), the metamaterial block behaves as a double negative material in the frequency range 9.70–10.24 GHz as evident from the effective electric permittivity and magnetic permeability obtained using homogeneous modeling (Fig. 17).

The validity of the effective metamaterial macrostructure is justified by comparing it with the detailed metamaterial structure.

The detailed metamaterial macrostructure is shown in Fig. 18(a). It forms a wedge shape composed of SRRs and wires. The unit cell of the detailed structure is also shown in Fig. 18(b).

The detailed metamaterial macrostructure characteristics can be observed from the dispersion diagram (Fig. 18(c)) of the unit cell (Fig. 18(b)). A passband in the frequency range between 9.9 GHz and 10.1 GHz is observed for backward wave while a passband between the frequency range between 11.6 GHz and 18 GHz is observed for the forward wave.

The effective macrostructure is a wedge shaped homogeneous structure with dimensions equivalent to the corresponding detailed metamaterial macrostructure (Fig. 19).

According to the electric field distribution of the effective metamaterial macrostructure shown in Fig. 20, there is a feeble transmission at 7 GHz, i.e., in the first frequency range between 7 GHz and 9.7 GHz where a vigorous reflection is observed. The transmission is increased in the central region of second double negative (DNG) band between 9.7.7 GHz and 10.24 GHz. The propagation of a backward wave is noticed inside the metamaterial wedge. The negative refraction can be observed from the field distribution. In frequency range between 10.24.24 GHz and 11.6 GHz, a feeble transmission is observed but significantly stronger than in the first frequency band. The minimum attenuation is noticed in the fourth double positive frequency band between 11.6.6 GHz and 18 GHz. A positive refraction can be observed from the field distribution at 15 GHz.

The electric permittivity and magnetic permeability are explained by the extracted Drude and Lorentz models, respectively, and are isotropic. The boundary conditions and excitations used for the numerical simulations are the same as those applied for the detailed macrostructure. The electric field distribution in the effective wedge at the same frequencies are similar to those of the detailed metamaterial macrostructure as reported in Lubkowski *et al.* (2009).

It is observed that the effective metamaterial model is authentic when compared to the detailed structure.

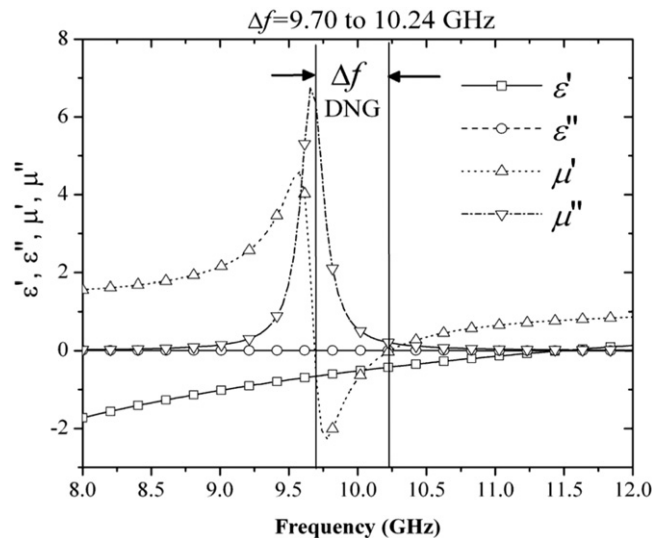


Fig. 17 Variation of effective material characteristics with frequency [re-occurrence from Ghatak, R., Goswami, C., Poddar, D.R., 2012. Investigation on resonance and radiation properties of rectangular microstrip antennas with partially filled metamaterial substrates and superstrates. International Journal of RF and Microwave Computer-Aided Engineering 421–574].

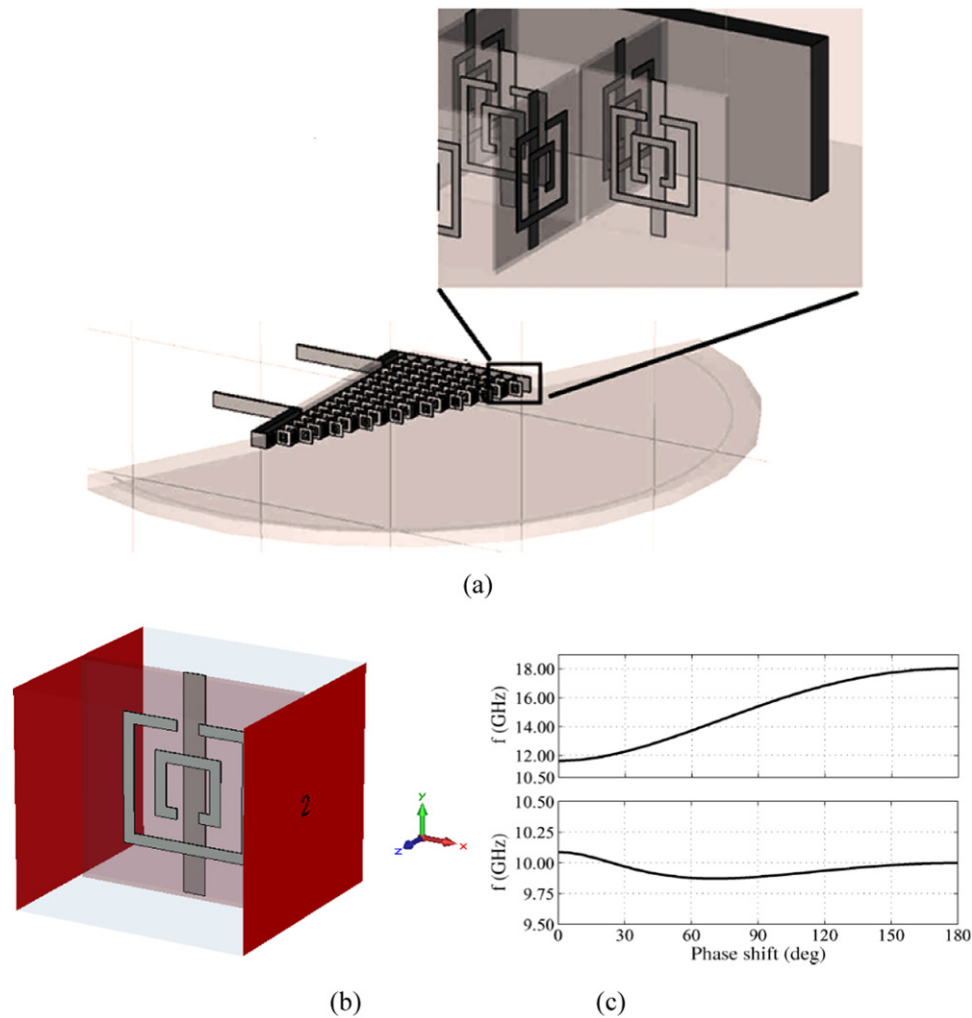


Fig. 18 (a) Detailed implementation of metamaterial macrostructure (b) unit cell (c) dispersion diagram [re-illustrated from Lubkowski, G., Bandlow, B., Schuhmann, R., Weiland, T., 2009. Effective modeling of double negative metamaterial macrostructures. IEEE Transactions on Antennas and Propagation 1136–1146].

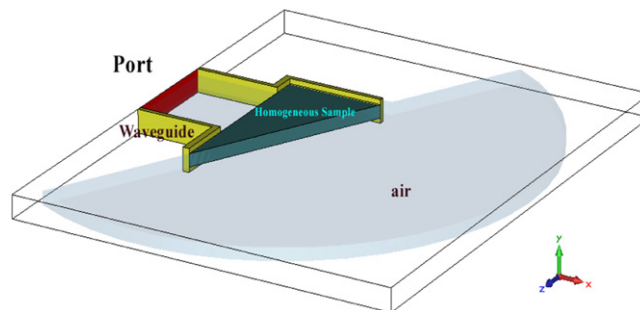


Fig. 19 Homogeneous effective implementation of metamaterial macrostructure [re-illustrated from Lubkowski, G., Bandlow, B., Schuhmann, R., Weiland, T., 2009. Effective modeling of double negative metamaterial macrostructures. IEEE Transactions on Antennas and Propagation 1136–1146].

The use of homogeneous model of metamaterial has been reported in [Ghatak *et al.* \(2012\)](#) for studying effect of resonance and radiation traits of microstrip patch antenna partially loaded with inhomogeneous substrates and superstrates consisting of μ -negative and double negative metamaterials. It is observed that the gain and resonant frequency is greatly influenced by size of μ -negative and double negative metamaterial regions.

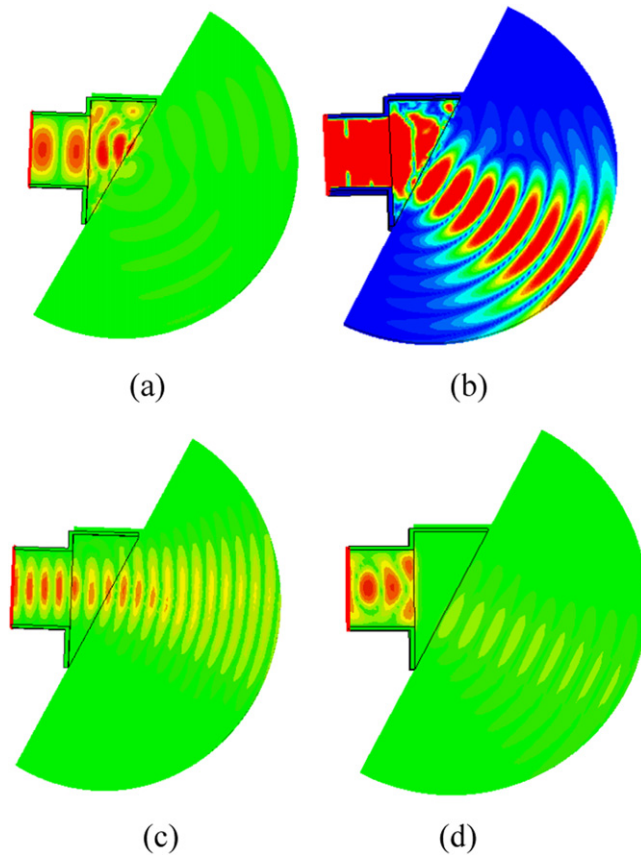


Fig. 20 Distribution of the electric field at different frequencies for the effective wedge structure (a) 7 GHz, (b) 10 GHz, (c) 11.5 GHz and (d) 15 GHz [re-illustrated from Lubkowski, G., Bandlow, B., Schuhmann, R., Weiland, T., 2009. Effective modeling of double negative metamaterial macrostructures. IEEE Transactions on Antennas and Propagation 1136–1146.].

CLRH TL Applications in Microwave Paradigm

The development of CRLH TL has paved the path in the realization of plethora of devices in the microwave paradigm. Some of the guided, radiated and refracted applications are discussed under following subsections.

Guided Wave Applications of CLRH TL

Zeroth order resonator (ZOR) is one of the interesting applications of CLRH TL where zero value of β can be obtained at a non zero frequency (Fig. 5(c) and (d)). Utilizing this property, one such type of resonator is reported in (Sanada *et al.*, 2003) and is shown in Fig. 21. At $\beta = 0$, there is no phase shift across the resonator as the phase shift is determined by $\varphi = -\beta d = 0$. It is also shown that the resonance is no dependent on the length of the structure but depends only on the reactive loading.

Moreover, CLRH TLs can also yield arbitrary operating frequencies in branch line couplers. In conventional branch line couplers, the operating frequencies are limited to its design frequency (f_1) and at their odd harmonics. However, in multiband wireless communication systems, the operating frequencies are separated by various non-harmonic frequencies. This drawback can be eradicated by the usage of CRLH TLs instead of RH TLs to produce an arbitrary second operating frequency (Lin *et al.*, 2003).

The advantage of CRLH TL based branch line coupler over RH TL based branch line coupler can be understood from the phase response diagram shown in Fig. 22.

As depicted from the phase-response curve, The CRLH TL's phase-response curve can intercept a desired pair of phases at any arbitrary pair of frequencies for dual-band operation by changing the phase slope and dc offset. A CRLH TL based branchline coupler reported in (Lin *et al.*, 2003) is shown in Fig. 23.

Apart from the above mentioned applications, CRLH metamaterials can also be applied in bandwidth enhancement and size reduction of microwave components.

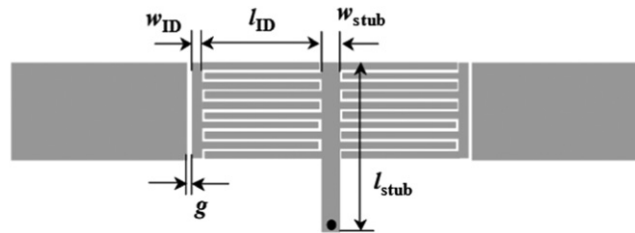


Fig. 21 Zeroth order resonator [re-illustrated from Sanada, A., Caloz, C., Itoh, T., 2003. Zeroth order resonance in composite right/left handed transmission line resonators. Proceedings of the Asia Pacific Microwave Conference. Seoul: IEEE Publishers, pp. 1588–1592].

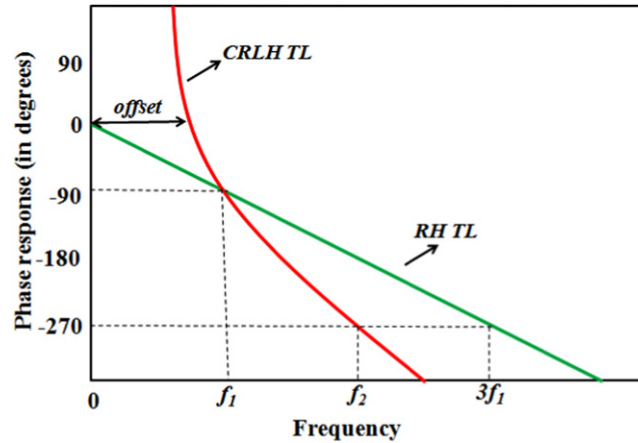


Fig. 22 The comparison of phase response of a RH TL and a CRLH TL [re-illustrated from Lin, I., Caloz, C., Itoh, T., 2003. A branch-line coupler with two arbitrary operating frequencies using left-handed transmission lines. IEEE MTT-S International Microwave Symposium Digest. IEEE Publishers, pp. 325–328.].

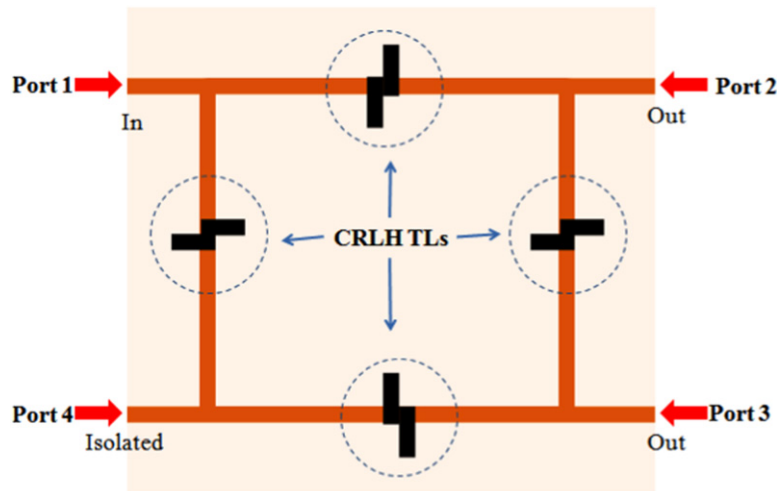


Fig. 23 Photograph of dual band branch line coupler with CRLH TL [re-illustrated from Lin, I., Caloz, C., Itoh, T., 2003. A branch-line coupler with two arbitrary operating frequencies using left-handed transmission lines. IEEE MTT-S International Microwave Symposium Digest. IEEE Publishers, pp. 325–328.].

Radiated Wave Applications of CLRH TL

The principle of zeroth order resonator discussed in the previous section can be utilized to realize a ZOR antenna (Sanada *et al.*, 2004) as shown in Fig. 24. The unit cell based on microstrip patch consists of an interdigital capacitor and a shunt meander line connected to a rectangular patch. The rectangular patch acts as a virtual ground plane. The size of the antenna can be considerably reduced to smaller than half of a wavelength since resonance does not depend upon the physical dimension of ZOR. In this type of designs, size of the antenna depends on reactive loading as shown in Fig. 24.

The concept of balanced CRLH TL can be extended in designing frequency scanned leaky wave (LW) antenna when perfectly matched to the air impedance (Liu *et al.*, 2000). A CRLH LW antenna can operate at its fundamental mode, because this mode consist of a radiation (or fast-wave) region in addition to a guided (or slow-wave) region as shown in Fig. 25(a). However, the RH based leaky wave antenna structures operates at higher order modes in order to radiate and hence require complex feeding structures.

The CRLH LW antennas are capable of continuous scanning from backfire to endfire angles unlike conventional LW antennas as explained using Fig. 25(b).

Metamaterial Inspired Antennas

The idea of utilizing resonant metamaterial object in the near field of an electrically small antenna to enhance its radiation characteristics was well established in (Ziolkowski and Kippel, 2005; Ziolkowski and Erentok, 2006). The theoretical model is such

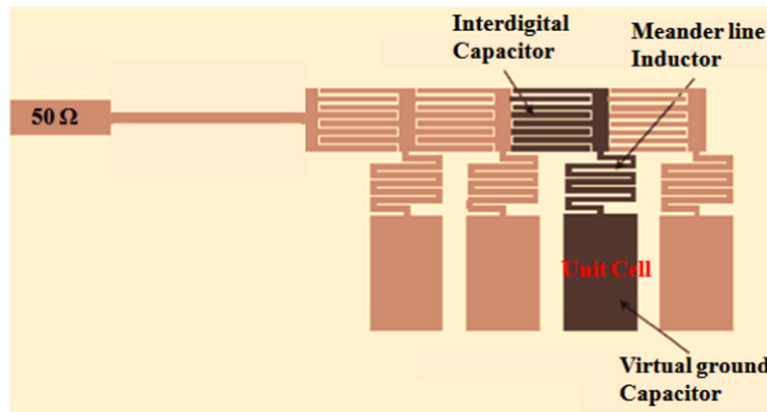


Fig. 24 Layout of a ZOR antenna [re-illustrated from Sanada, A., Kimura, M., Awai, I., Caloz, C., Itoh, T., 2004. A planar zeroth order resonator antenna using left-handed transmission line. Proceedings of the 34th European Microwave Conference. IEEE Publishers, pp. 1341–1344.].

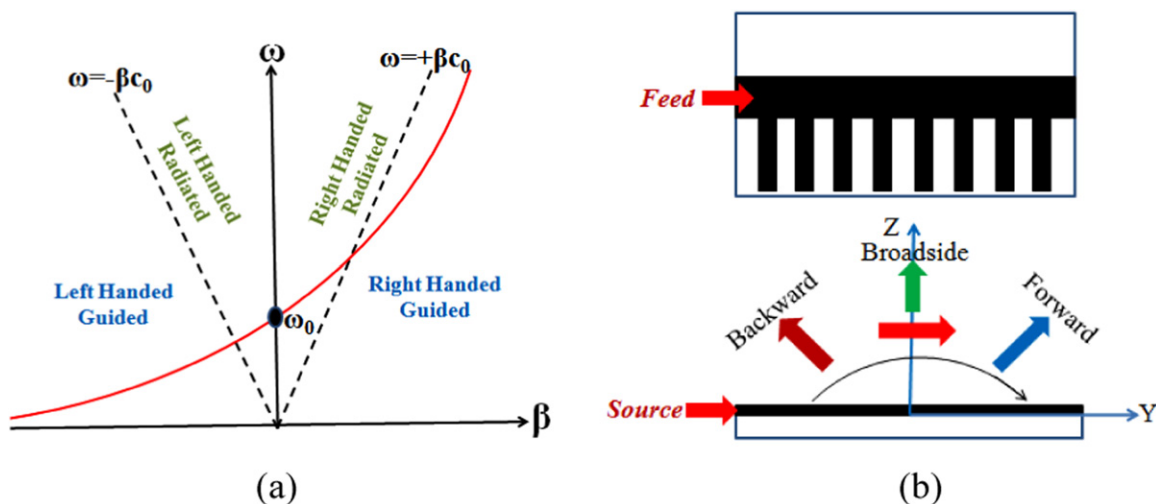


Fig. 25 (a) Dispersion diagram showing guided and radiation regions in leaky wave antenna and (b) Scanning operation of CRLH LW antenna [re-illustrated from Liu, L., Caloz, C., Itoh, T., 2000. Dominant mode (DM) leaky wave antenna with back fire-to-endfire scanning capability. Electronic Letter 1414–1416.].

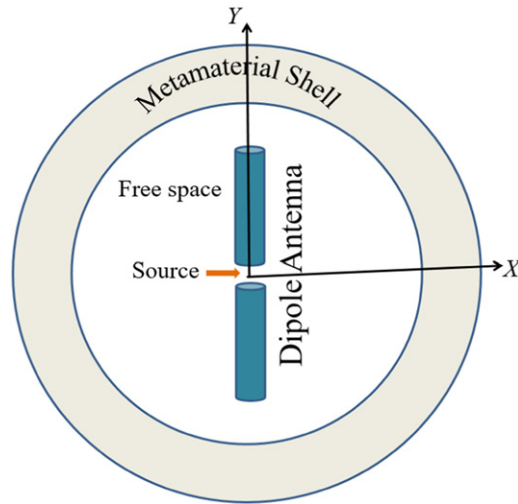


Fig. 26 A center fed dipole antenna surrounded by an ENG shell [re-illustrated from Ziolkowski, R.W., Erentok, A., 2006. Metamaterial based efficient electrically small antennas. IEEE Transactions on Antennas and Propagation. 2113–2130.].

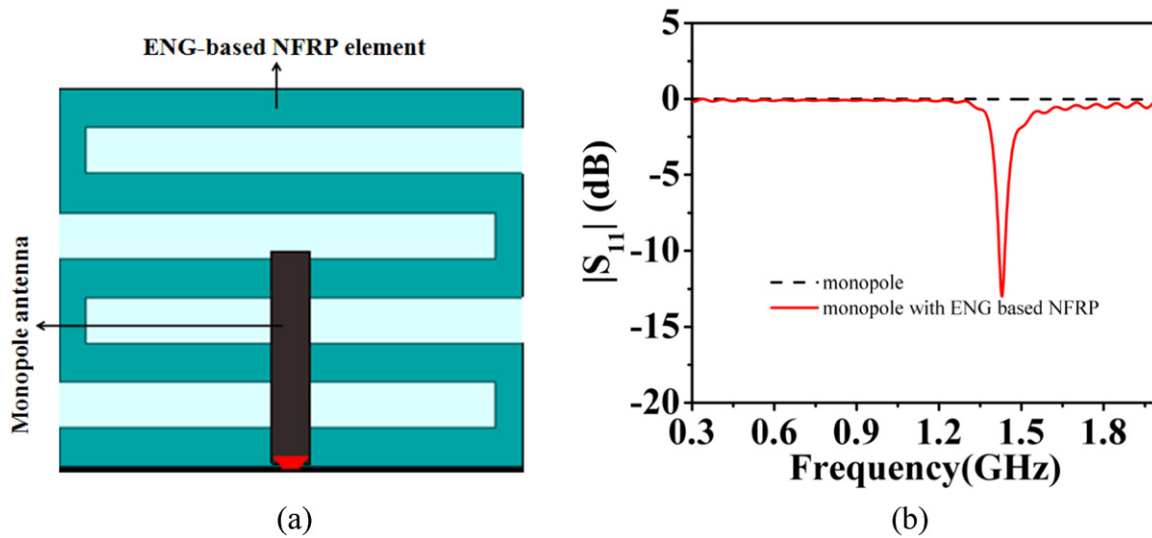


Fig. 27 (a) ENG based NFRP antenna (b) $|S_{11}|$ characteristics showing resonance in presence of meander line NFRP [re-illustrated from Erentok, A., Ziolkowski, R.W., 2008. Metamaterial-inspired efficient electrically small antennas. IEEE Transactions on Antennas and Propagation. 691–707.].

that it encloses a radiating dipole with double negative or single negative spherical metamaterial shells. One such design was reported in (Ziolkowski and Erentok, 2006) and is shown in Fig. 26.

It is described in (Ziolkowski and Erentok, 2007), that with an active ENG shell, the bandwidth can be increased considerably beyond Chu (2008) and Thal (2003) limits. However, the practical problem with the MTM-shell concept is the need of extremely small sized unit cells. But the smallest unit cells fabricated to date are $\lambda_{res}/75$ at 400 MHz (Erentok *et al.*, 2007). In (Erentok and Ziolkowski, 2008), it was shown that, a near field resonant parasitic (NFRP) element constructed using a single metamaterial unit cell is acceptable to achieve the desired radiation performance. The resulting radiating system were therefore termed as metamaterial inspired antennas rather than metamaterial based antennas because a single metamaterial unit cell was used instead of a bulk medium. An electrically small printed monopole antenna radiating in presence of a meander line is shown in Fig. 27(a). The 2D meander line is an epsilon negative metamaterial which provides necessary inductance for impedance matching of the capacitive monopole antenna to the source. The $|S_{11}|$ characteristics in Fig. 27(b) reveals that the monopole resonates at 1.4 GHz in presence of meander line NFRP.

Metamaterial inspired subwavelength resonators also finds application in band notch antenna designs. A metamaterial inspired electric LC based multimode resonator (MMR) is utilized in (Gorai and Ghatak, 2019) for creating band notches at 5.5 GHz and 8.1 GHz (Fig. 28). Metamaterial inspired split ring resonator is also used in (Zhang *et al.*, 2008) for creating band notches.

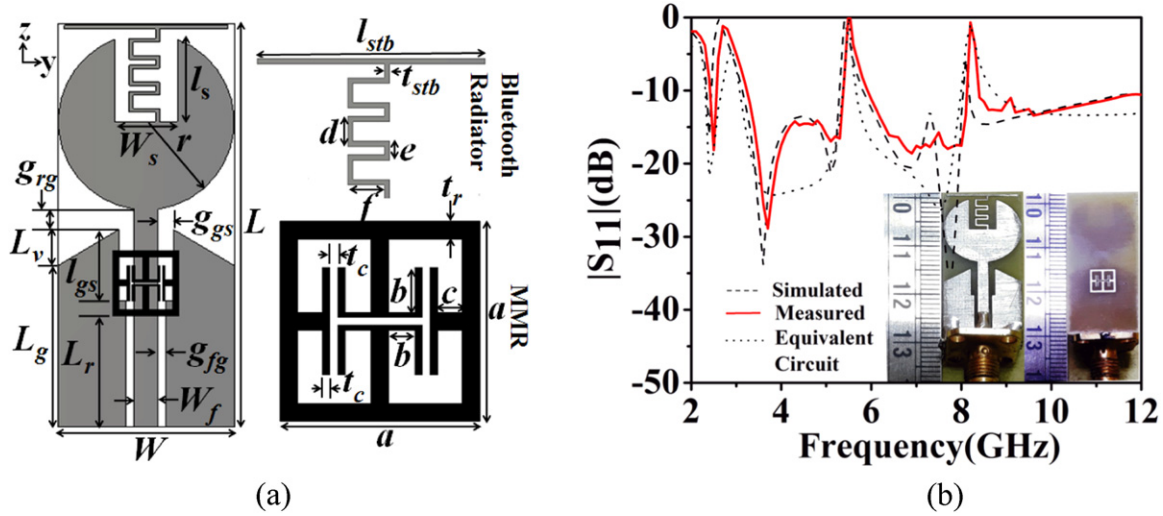


Fig. 28 (a) Metamaterial based MMR loaded in UWB monopole (b) $|S_{11}|$ characteristics showing band notches due to MMR [re-occurrence from Gorai, A., Ghatak, R., 2019. Multimode resonator-assisted dual band notch UWB antenna with additional bluetooth resonance characteristics. IEEE Transactions on Microwaves, Antennas & Propagation (13), 1854–1859.].

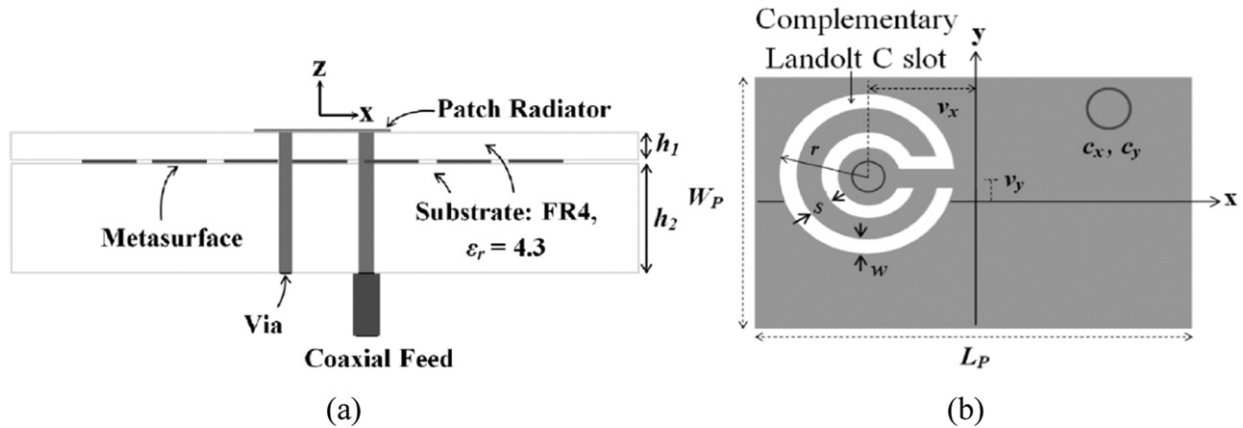


Fig. 29 (a) Cross sectional view of the CP antenna (b) Complementary Landolt C-shape slot loaded rectangular patch [re-occurrence from Jash, S.S., Goswami, C., Ghatak, R., 2019. A low profile broadband circularly polarized planar antenna with an embedded slot realized on a reactive impedance surface. AEU-International Journal of Electronics and Communication 62–72.].

Antennas Loaded With Metasurface

Metasurface is a subclass of metamaterials, demands increasing attention in application in microwave circuits and antennas (Zhang *et al.*, 2003). The metasurfaces can be classified into several types, such as the reactive impedance surface (RIS) composed by periodic metallic patches (Saenz *et al.*, 2008), the mushroom-like high-impedance or artificial magnetic conductor (AMC) or EBG structures (Zhu and Langley, 2009), and the uniplanar compact photonic band gap (UC-PBG) surface (Yang *et al.*, 1999). The AMC or EBG has capability to produce zero reflection phase and are able to suppress the surface wave. There are various applications of metasurface to enhance the radiation performance of antennas in different aspects.

A small sized and broadband slotted microstrip patch antenna on RIS is proposed to be circularly polarized (CP) planar antenna in (Jash *et al.*, 2019). The cross-sectional view of the CP microstrip antenna is depicted in Fig. 29, metasurface is shown in Fig. 30 and the unit cell is shown as an inset of Fig. 31. The PEC and PMC boundaries are defined along y and x direction of the RIS unit cell. As depicted in Fig. 31, the reflection phase becomes zero at 6.67 GHz, indicating that RIS resonates around 6.67 GHz. The impedance bandwidth obtained from the $|S_{11}|$ characteristics in Fig. 32(a) ranges from 3743 GHz to 5976 GHz. Moreover, the axial ratio bandwidth is found to be 1387 MHz as depicted in Fig. 32(b).

Another work reported in (Hussain *et al.*, 2020) shows that impedance bandwidth and axial ratio bandwidth is enhanced on addition of metasurface (Fig. 34). Fig. 33 shows the CP antenna loaded with metasurface.

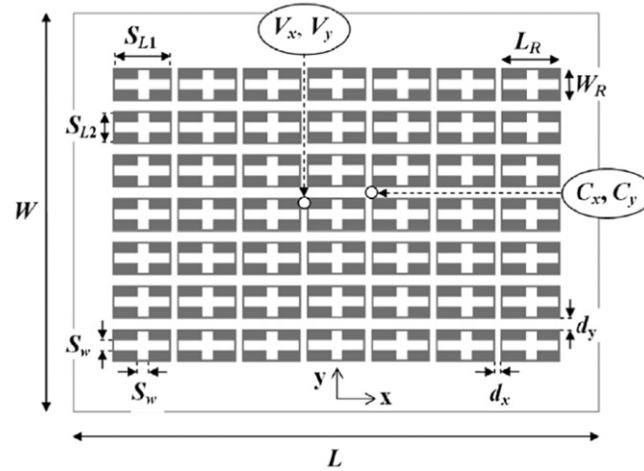


Fig. 30 Metasurface with 7×7 rectangular cross slotted unit cells [re-occurrence from Jash, S.S., Goswami, C., Ghatak, R., 2019. A low profile broadband circularly polarized planar antenna with an embedded slot realized on a reactive impedance surface. AEU-International Journal of Electronics and Communication 62–72.].

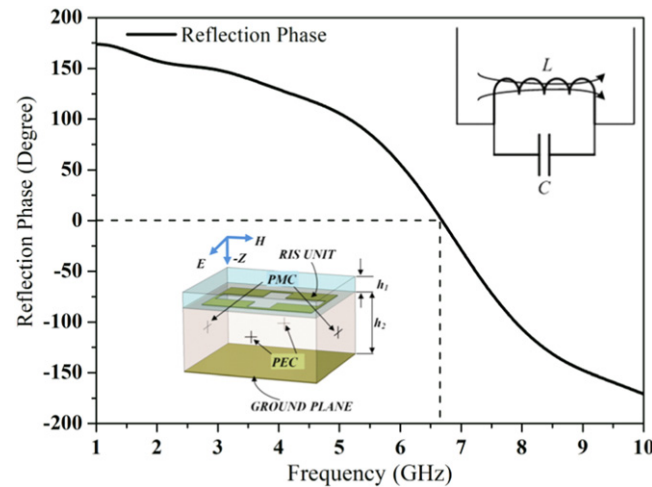


Fig. 31 Reflection phase diagram of the unit cell (inset: unit cell) [re-occurrence from Jash, S.S., Goswami, C., Ghatak, R., 2019. A low profile broadband circularly polarized planar antenna with an embedded slot realized on a reactive impedance surface. AEU-International Journal of Electronics and Communication 62–72.].

The high impedance surfaces or magnetic mirrors also find application in high frequency absorbers. Generally, metamaterial surfaces are two dimensional periodic arrangements of many small unit cells. These properties of these surfaces, also termed as frequency selective surfaces are greatly influenced by the shape and size of these small metamaterial unit cells. Placing these types of frequency selective surfaces over perfectly conducting plates can over certain band of frequencies can yield a high impedance ground plane. A proper placement of a resistive sheet on top of this surface can result in an efficient absorber for incident electromagnetic energy (Engheta, 2002) as shown in Fig. 35.

Metamaterial in Energy Harvesting

Energy harvesting is not a new concept, where the process is to generate electrical energy from the surrounding conditions using some energy conversion mechanism as depicted in Fig. 36. Generally, output obtained directly is AC which must be converted to DC. Out of many conversion media, metamaterials came out to be an efficient media for energy harvesting when compared to naturally available materials. Owing to the properties like negative refractive index and evanescent wave amplification, electromagnetic metamaterials can be used for electromagnetic energy harvesting for achieving higher performance.

A complete microwave wireless power transmission consists of three parts: for conversion from DC power to microwave power, receiving microwave power by antennas, finally conversion of microwave power to DC output power. An integral

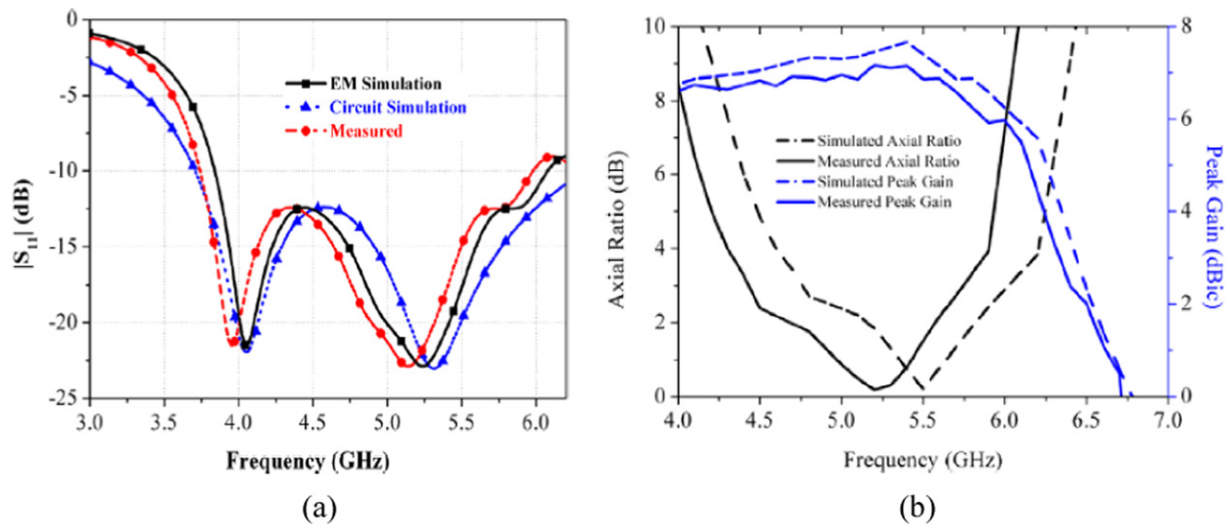


Fig. 32 (a) $|S_{11}|$ characteristics of the CP antenna (b) Axial ratio and gain of the CP antenna [re-occurrence from Jash, S.S., Goswami, C., Ghatak, R., 2019. A low profile broadband circularly polarized planar antenna with an embedded slot realized on a reactive impedance surface. *AEU-International Journal of Electronics and Communication* 62–72.].

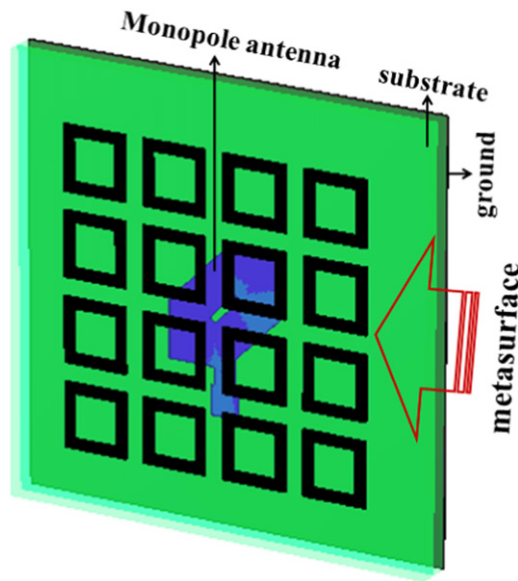


Fig. 33 A metasurface antenna [re-illustrated from Hussain, N., Jeong, M., Abbas, A., Kim, N., 2020. Metasurface-based single-layer wideband circularly polarized MIMO antenna for 5G millimeter-wave systems. *IEEE Access*. 130293–130304.].

part of such systems is rectenna (rectifying antenna). Some significant works involving array of rectennas to achieve long distance microwave power transmission are reported (McSpadden and Mankins, 2002; Bragg *et al.*, 2013). However, difficulty in the design of complex feeding, and coupling of antenna elements limits the performance. Such limitations are overcome by metamaterial inspired rectenna designs. The first metamaterial-based structure to obtain increased microwave power transmission was reported in (Alu *et al.*, 2006), where a metamaterial cover is used to enhance the power transmission (Fig. 37).

Summary

The article delves in to the various aspects of artificially realized periodic structures that behave as a homogeneous medium upon placing the unit structures with spacings much smaller than the impinging electromagnetic wave interacting with the medium. These materials have found numerous applications in high frequency electronics spanning antenna, circuits to absorbers. Basics of

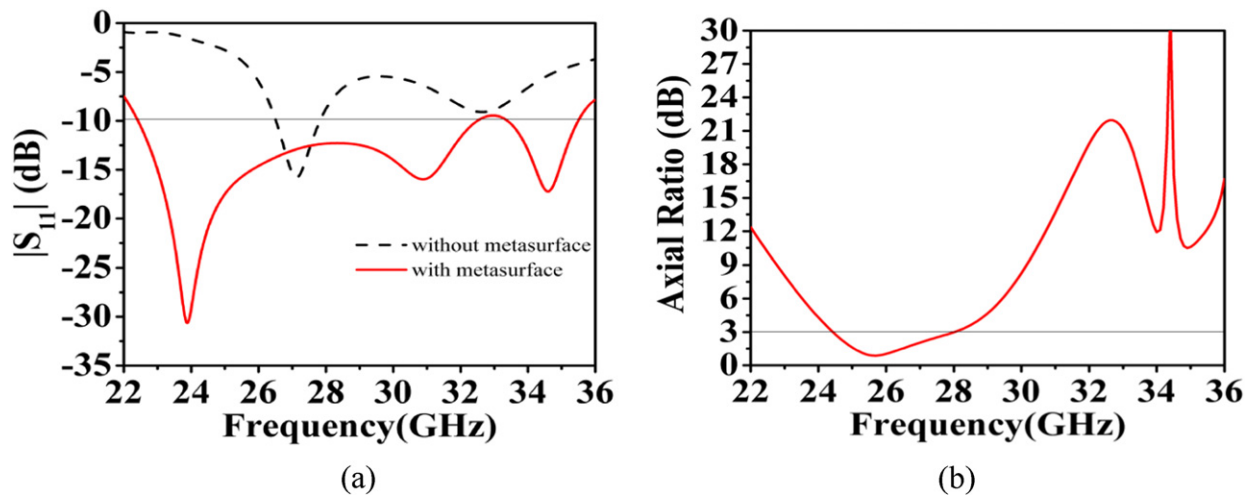


Fig. 34 (a) Comparison of $|S_{11}|$ characteristics of the antenna with metasurface and without metasurface (b) Axial ratio of the metasurface Antenna [re-illustrated from Hussain, N., Jeong, M., Abbas, A., Kim, N., 2020. Metasurface-based single-layer wideband circularly polarized MIMO antenna for 5G millimeter-wave systems. IEEE Access. 130293–130304.].

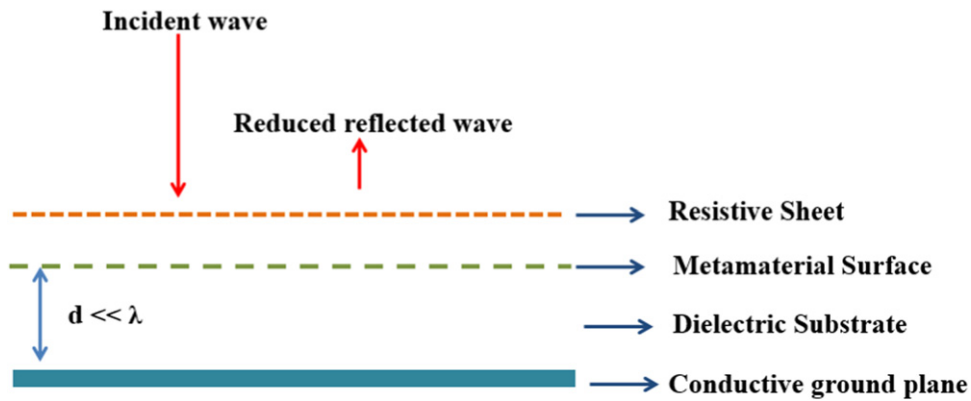


Fig. 35 Application of metamaterial surfaces in thin absorbing screens.

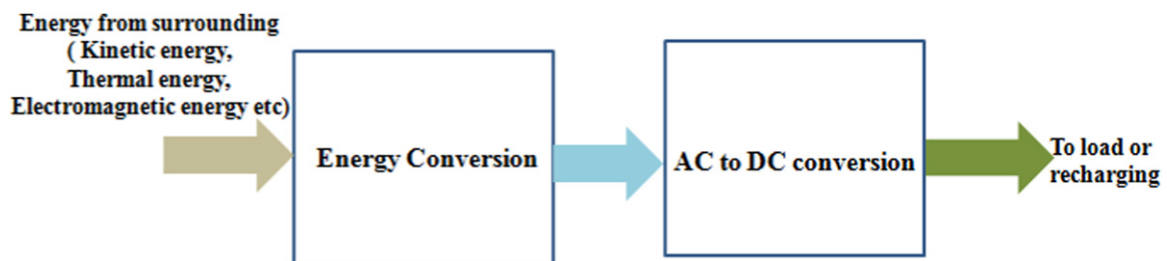


Fig. 36 Process of energy harvesting.

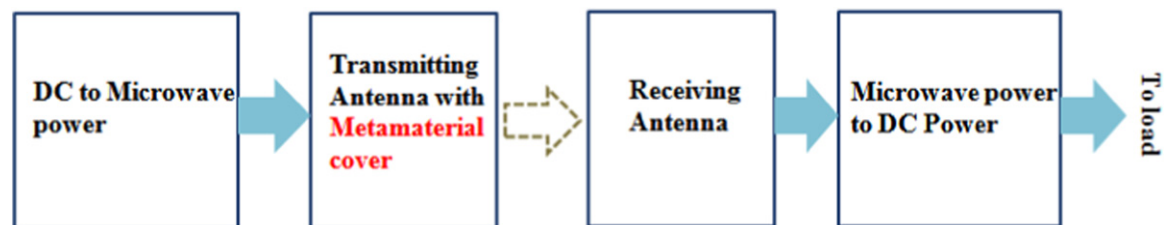


Fig. 37 Use of Metamaterial cover in microwave wireless power transmission.

the realization mechanism, characterization and its efficacy in some high frequency electronics paradigm are revisited in this article. The discussion also includes the two dimensional versions of the volumetric metamaterials as well as some stand alone usage of the basic building blocks of the unit cell in realization of metamaterial inspired electromagnetic systems. Metamaterial in brevity has found numerous application in various frequency ranges of the electromagnetic spectrum. The realization at all these domains depends on the fabrication complexities that has inculcated more interest in this paradigm.

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Search of Potential Dopants and its Effect on TiO₂-Based Low Voltage Varistor Materials

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Abstract

Varistors are electroceramic devices used as surge protectors for electrical and electronic systems. At present low-voltage varistors are in demand due to miniaturization of the microelectronic circuits. In this research, the electrical properties of titanium dioxide (TiO₂) doped with tantalum pentoxide (Ta₂O₅), tungsten trioxide (WO₃), silicon dioxide (SiO₂) and bismuth oxide (Bi₂O₃) and fired at different temperatures were investigated for low voltage applications. The adequate amount of dopants at suitable sintering temperature had beneficial effect in improving the properties of TiO₂. High green and fired density, high Vickers hardness and compressive strength were achieved with the composition of 0.5% SiO₂, 0.5% Ta₂O₅, 0.25% WO₃, and 0.5% Bi₂O₃ when sintered at 1400°C. The average grain size was also increased with the dopants system and significantly lowered the breakdown voltage (910 mV/mm), making it suitable for low voltage application. Furthermore, the current-voltage characteristic of the TiO₂ revealed a significantly high value of nonlinearity of 16.5 and low clamping ratio. Moreover, higher permittivity of 4.89×10^4 and low dissipation factor at 100 Hz were achieved with the new composition. Hence, it was possible to produce a new TiO₂ based varistor material with enhanced properties and reliability. The fabrication was simulated using Silvaco software which showed higher value of 21.4 for the nonlinear coefficient with the same composition. The composition of 0.5 wt% Ta₂O₅ + 0.5 wt% SiO₂ + 0.25 wt% WO₃ + 0.5 wt% Bi₂O₃ when sintered at 1400 °C with two hours of holding time provided significantly improved characteristics.

Key Term Definitions

The key term dopants are used in varistor fabrication where intentional addition of impurities is required, since the base material alone can not exhibit the required characteristics of a varistor. The enhancement of properties is very much dependent on the type and concentration of dopants used. The addition of dopants results crystal imperfections within grains as well as grain boundaries. Free electrons and holes are created to conduct current, thereby providing protection from sudden surges.

The key term non-linear coefficient which is designated as α is the critical parameter to characterize the varistor. As it is the logarithmic ratio of current over voltage, hence the magnitude varies with current density. In the non-linear region the higher value of α corresponds to the lower clamp ratio, thereby, providing better protection due to the lower increase of voltage at higher current level.

Introduction

Varistors are surge protectors against excessive transient voltage in electrical and electronic devices. It is a semiconducting device with similar characteristics to a diode which can limit the voltages in both polarities (Karim *et al.*, 1997). Thus it provides reliable and economical protection against high voltage surges. It can absorb and suppress higher voltage surges when it is exceeding its normal operating range. In general, varistor acts as an insulator during normal operation below its breakdown voltage and shunts away certain limit of current to travel across the circuit when voltage is excessive (Dhage *et al.*, 2007; Bruno *et al.*, 2003; Littelfuse, 2014; He, 2019).

The performance of varistor material is grain and grain boundary phenomena which are formed during sintering process. Grains are separated by grain boundaries and provide a sort of reverse bias p-n junction type behavior which blocks conduction at low voltages and is the source of nonlinear conduction at high voltages (Harnden *et al.*, 1972; Ivetića *et al.*, 2018). The grain boundaries possess surge withstanding capability for which the conduction paths are dominated (Aref *et al.*, 2010). Depending upon applications, varistors are classified as high voltage and low voltage varistors. High voltage varistors are used in transmission lines and transformers. Low voltage varistors on the other hand are used in electrical and electronic devices.

There is a need for low voltage limiters (varistors) as more devices are converted from microelectronics to nanoelectronics (Li *et al.*, 2003). The most common high-voltage varistor materials used in the industry today are predominantly based on zinc oxide (ZnO) and some small-scale silicon carbide (SiC). ZnO varistor displays high nonlinear coefficient, however, because of its low permittivity it is unable to absorb spark, and therefore, it is not suitable for the low voltage application (Navale *et al.*, 2007). As for the SiC varistor materials, it has lower nonlinear coefficient compared to ZnO materials. Thus, SiC varistor materials do not exhibit requisite electrical properties.

Low voltage varistors should exhibit nonlinear current-voltage (I–V) relationship with enhanced electrical properties such as high nonlinear coefficient, low breakdown voltage, high dielectric constant and minimal leakage current. Pure titanium dioxide (TiO₂) in rutile phase is a non-stoichiometric *n*-type semiconductor with linear I–V behavior and is an emerging varistor material that can meet the demands for today's modern electronic devices. In this study, the dopants added to TiO₂ based varistor material are Ta₂O₅, WO₃, Bi₂O₃ and SiO₂. The effect of tantalum pentoxide (Ta₂O₅) on TiO₂ varistors was investigated and it was observed that the addition of Ta₂O₅ enhanced the nonlinear coefficient within the range of 25–30, thereby, having the potential to be a

voltage surge protector (Navale *et al.*, 2007). Tantalum also leads to low breakdown voltage and high permittivity (Li *et al.*, 2003). The addition of WO₃ increases the electrical resistivity in the SnO₂ based varistor material (Perazolli *et al.*, 2005). In another research (Su *et al.*, 2003), the addition of WO₃ to TiO₂ varistor yielded nonlinear coefficient 9.6. Apart from this result, the high density of WO₃ improves the strength of the material. The addition of Bi₂O₃ is to improve the sintering process of the material, and it was found that the oxides tend to segregate at the grain boundaries and alter the electrical characteristics (Bomio *et al.*, 2004). Brown and Grannemann (1978) investigated the C–V characteristics of Ti–SiO₂ capacitors and found that the dielectric constant can be improved ranging between of 4–40. The addition of SiO₂ leads to lower capacitance and lower leakage current.

Sintering temperature also has significant effect on the non-linear properties and breakdown voltage. As temperature increases, breakdown voltage decreases accordingly. It promotes the transportation of ions and formation of the grain boundaries. The behavior of nonlinearity of the current-voltage characteristic can be related to the Schottky barrier height (Navale *et al.*, 2007; Abdullah *et al.*, 2012b; Nahm, 2008; Huang *et al.*, 2020). Numerous researchers have focused on ways to suppress the transient voltage by increasing the sintering temperature of the varistor to decrease the breakdown voltage (Abdullah *et al.*, 2012b; Xu *et al.*, 2009; Nahm, 2008; Leach *et al.*, 2000). However, porosity would increase resulting from the evaporation at exorbitant temperature that cause the decrease in barrier height at the grain boundaries. Therefore, to overcome this problem, selection of the suitable dopants (additives) and sintering condition would be the major governing parameters to dictate the electrical properties as well as mechanical strength and the microstructure of TiO₂. Hence, in this research the combination of various dopants and sintering temperature were considered to monitor their effect on physical and electrical properties. Beside these mechanical strength and microstructures were evaluated to generate high performance low voltage varistor materials possessing improved reliability.

Experimental

The varistor material using TiO₂ powder as a base material was prepared with four different dopants and composition of varistor powder is shown in Table 1. Commercially available ceramic powder was used for research. TiO₂ of 99.8% purity was bought from Merck (USA), whereas, all the four dopants Ta₂O₅, WO₃, Bi₂O₃ and SiO₂ were obtained from Sigma Aldrich Corporation (USA). The percentage of Bi₂O₃ and WO₃ was fixed to 0.5% and 0.25%, respectively. The fixed percentage of Bi₂O₃ and WO₃ was selected based on the available information (Xu *et al.*, 2009; Nahm, 2010; Anas *et al.*, 2010; Bomio *et al.*, 2004; Pianaro *et al.*, 1999). Conventional ceramic processing technique was adopted. The powders were mixed and ball milled with zirconia balls as the milling media and ethanol as the solvent. The prepared slurry was dried at 60°C for 24 h, and sieved to achieve green

Table 1 Composition and sintering temperature of TiO₂ based varistor powder

Temperature	Sample identification	Experimental identification	SiO ₂ (wt%)	Ta ₂ O ₅ (wt%)	WO ₃ (wt%)	Bi ₂ O ₃ (wt%)	TiO ₂ (wt%)
1300	A	1	0.1	0	0.25	0.5	99.15
	B	2	0.3	0	0.25	0.5	98.95
	C	3	0.5	0	0.25	0.5	98.75
	D	10	0.1	0.25	0.25	0.5	98.9
	E	11	0.3	0.25	0.25	0.5	98.7
	F	12	0.5	0.25	0.25	0.5	98.5
	G	19	0.1	0.5	0.25	0.5	98.65
	H	20	0.3	0.5	0.25	0.5	98.45
	I	21	0.5	0.5	0.25	0.5	98.25
1350	A	4	0.1	0	0.25	0.5	99.15
	B	5	0.3	0	0.25	0.5	98.95
	C	6	0.5	0	0.25	0.5	98.75
	D	13	0.1	0.25	0.25	0.5	98.9
	E	14	0.3	0.25	0.25	0.5	98.7
	F	15	0.5	0.25	0.25	0.5	98.5
	G	22	0.1	0.5	0.25	0.5	98.65
	H	23	0.3	0.5	0.25	0.5	98.45
	I	24	0.5	0.5	0.25	0.5	98.25
1400	A	7	0.1	0	0.25	0.5	99.15
	B	8	0.3	0	0.25	0.5	98.95
	C	9	0.5	0	0.25	0.5	98.75
	D	16	0.1	0.25	0.25	0.5	98.9
	E	17	0.3	0.25	0.25	0.5	98.7
	F	18	0.5	0.25	0.25	0.5	98.5
	G	25	0.1	0.5	0.25	0.5	98.65
	H	26	0.3	0.5	0.25	0.5	98.45
	I	27	0.5	0.5	0.25	0.5	98.25

powder. The green powder was compacted into a disc shaped pallet of 20 mm diameter using hydraulic press machine (NHP-25T) at 2.79 MPa.

The green pellets were sintered at 1300, 1350, and 1400°C with a holding time of 2 h in a high temperature sintering furnace (ModuTemp). The sintered pellets were polished using SiC paper of 120, 240, 600, 800 and 1200 grades, respectively and finally diamond polished using 6 and 1 µm diamond paste to obtain a reflective surface with a polishing machine (Impitech Europe grinder-polisher). Silver paste was applied on the reflective surface of the pellet for conducting electrical characterization. The I-V plot was obtained using Keithley 6212A Electrometer from where the nonlinear coefficient, clamping ratio, and breakdown voltage were calculated. Watt-loss was determined at 80% of the breakdown voltage (Pianaro *et al.*, 1999). Permittivity and dissipation factor were measured using Alpha-A High Performance Modular Measurement over the range of frequency between 100 Hz and 4 MHz at room temperature. The samples were put in the samples holder and the test was performed under an oscillation voltage of 1 V.

The software used to obtain the dielectric measurement was WinDETA V5.55. To understand further the behavior of varistor with the variation of dopants and sintering temperature, permittivity and dissipation factor were measured using the same equipment. The prepared samples were characterized by evaluating green and fired density, Vickers Hardness, compressive strength, microstructure and electrical performance. The average grain size was calculated from the micrograph using the line intercept technique.

Simulation Using Silvaco Software

Silvaco Software is a modeling tool for electronic devices. Most commonly used for modeling metal-oxide-semiconductor field-effect transistor (MOSFET). Silvaco consists of two main soft wares, ATHENA which is used as a 2D process simulator and ATLAS which is the device simulator. Semiconductors have charge transport which is influenced by scattering of phonon. The Silvaco Software is able to simulate and model any kind of semiconductor. Silvaco Software has graphical user interface (GUI) which enables the user to see the outcome of the fabrication and result. The coding can be easily adjusted by using Silvaco and it also provides insights on the electrons work, it is predictive and it is able to capture the knowledge and translate it into reality (Vasileska and Goodnick, 2006). Silvaco TCAD is used in studying the electrical characteristics in a MOSFET, BJT, diode, image sensor and solar cell application (Vasileska and Goodnick, 2006).

Creating Initial Substrate

First, the grid is initialized so that the different concentration of material can be added without any complications. Besides that, it also controls the accuracy and save time during simulation. Initialization also determines how small the device can be. In short, grid initialization acts like borders for the structure. Initializing the grid has to be done accurately or the electrical properties of the device will be affected. The substrate preparation was done using crystallized silicon with $\langle 100 \rangle$ orientation. Fig. 1 depicts the initialization of the grid. After grid initialization, the base material was created. Options available from Silvaco Software interface are Silicon and Titanium. The base material used for this research is Titanium.

Deposition and Etching Material

The dopants used from the interface are SiO₂, Ta₂O₅ and WO₃. All these materials are found in the library. However, Bi₂O₃ was not in the library. Hence, a new material has to be created in ATLAS with a complete structure. Fig. 2 depicts the dopants deposited at the base material.

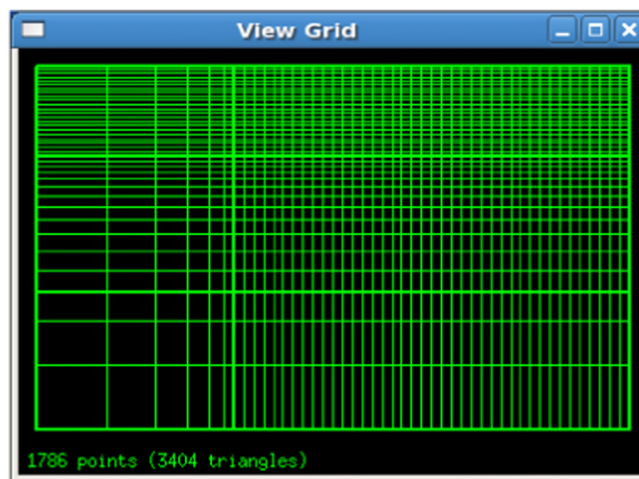


Fig. 1 Initialization of the grid.

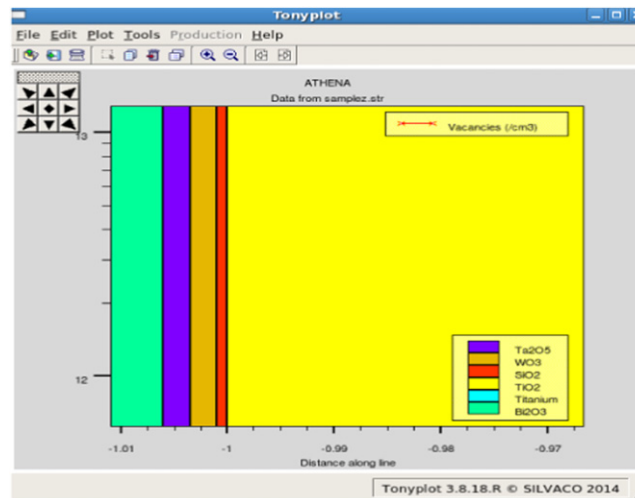


Fig. 2 Dopants deposited on the base material.

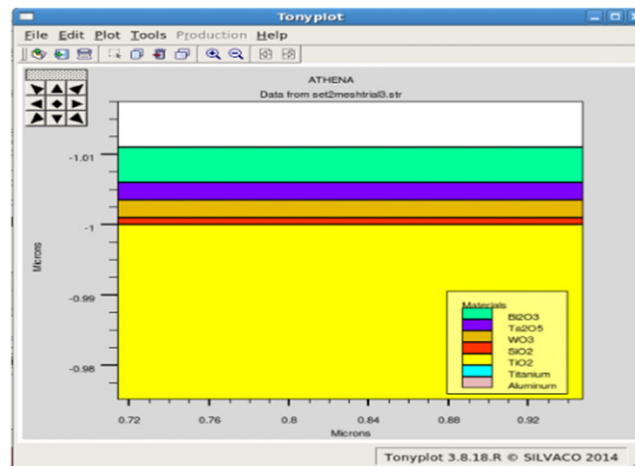


Fig. 3 Electroded structure.

Deposition was followed by etching the structure to the left. Etching is used for switching from 1D to 2D. The structure was metalized with Aluminum to create an electric circuit. Electrodes, anode and cathode are placed on the top of the material and the bottom of the material for electrical characterization. The electroded samples (Sapna, 2012) containing dopants for the TiO_2 varistor are presented in Fig. 3.

Simulator: ATLAS

ATLAS is a physically based device simulator which is not very common among engineers as it is complex. ATLAS is usually followed after ATHENA fabrication. However, ATLAS can run independently without fabrication from ATHENA. Besides that, ATLAS is also capable of interfacing with DevEdit. ATLAS is used to simulate the physical structure and produce electrical characteristics of the device. ATLAS produces three types of output files. The first type of output is to give the error warnings. The second type is the log file which stores all the terminal voltages and currents from the semiconductor device. The third type is output file to the solution after the calculation has been made. Fig. 4 shows the inputs and outputs of ATLAS (Yee, 2012).

2D Simulation

ATLAS starts off by defining a structure for the device and it is interfaced from ATHENA. The process of creating a new varistor using Silvaco requires additional steps as it was not built in the system. ATLAS simulation needs to follow the processing steps as given in Table 2.

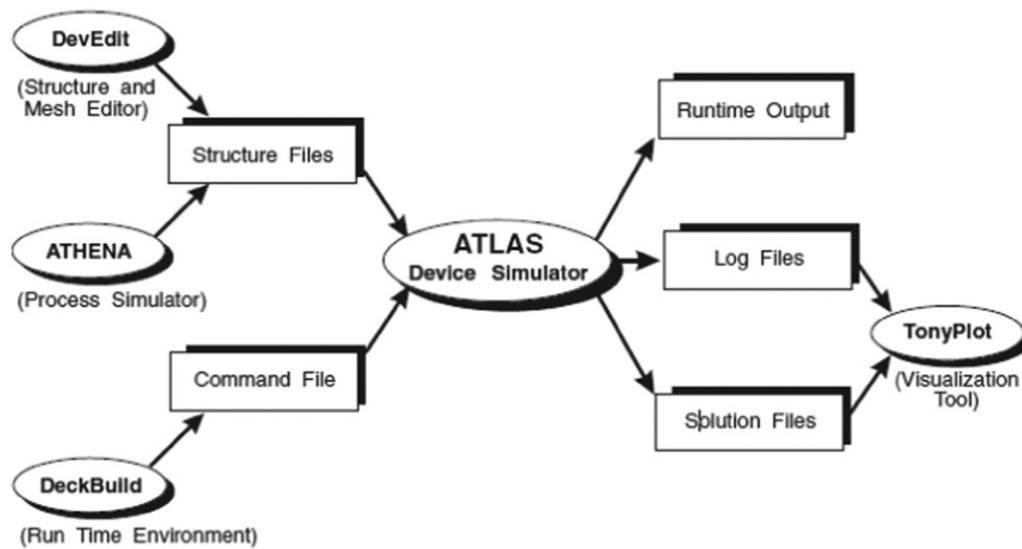


Fig. 4 Inputs and outputs of ATLAS.

Table 2 ATLAS processes

Process Steps	Functions
Structure Specification	(1) Mesh (2) Region (3) Electrode (4) Doping
Model Specification	(1) Material (2) Models (3) Contact (4) Interface
Numerical Method Selection Solution Specification	Method (1) Log (2) Solve (3) Load (4) Save
Result Analysis	(1) Extract (2) Tonyplot

Structure Specification

There are many ways to define the structure. The first is by reading from an existing file. The structure used for this program is ATHENA. Both ATHENA and ATLAS can run under DeckBuild (Silvaco Inc., 2012). Therefore, interface between the two softwares was done easily. The depositing of material was done in ATHENA. Besides that, the electrodes to conduct electricity were also conducted in ATHENA. For this research, the electrode was placed on the top and bottom of the structure. The space-mult syntax was used as a scaling factor. For mesh specification, the x.mesh and y.mesh was designed in ATLAS. A non-uniform mesh was being used because of the different composition of materials. The mesh was designed in a way that it does not overlap. Overlapping can make the system non-functional. As a result error messages will be generated.

Model Specification

To modify the characteristics of the structure, models for specific need to be created to obtain the desired results. ATLAS allows current boundary condition which is essential for a varistor. Besides that, a new material which is not found in the library is Bi₂O₃. Therefore, Bi₂O₃ was added by adding the properties. Shockley Read Hall (SRH) recombination is used and the new material allows to have properties such as bandgap (EG300), low field electron mobility (MUN), low field hole mobility (MUP),

conduction band density (NC300), valence band density (NV300) and permittivity (Silvaco Inc., 2012). The model used to calculate this device is Boltzmann because it is the default model. There are other models which can be used in ATLAS such as Fermi-Dirac (FERMI) distribution, incomplete ionization (INCOMPLETE), silicon ionization model (IONIZ), band gap narrowing (BGN), concentration dependence (CONMOB), and many more.

Numerical Method Selection

There are three types of method to choose from. First is the Newton Method. The Newton Method solves linearized version of the nonlinear system. The advantage of Newton Method is that it converges quickly. Besides that, there is also the Gummel Method which is used to solve small linear problems. It cannot be used for current boundary conditions. Since it is used to solve small linear problems, this method converges slowly. Apart from these two methods, there is also the Block Method which is used in lattice spacing and energy balance equation. It can also be used for non-isothermal drift diffusion (Silvaco Inc., 2012). In this research, the Newton Method is used as it is able to solve nonlinear problems and the characteristic of the varistor is nonlinear.

Solution Specification

After the method of calculation has been chosen, the I-V characteristics are then converted into a graph form where it is loaded and saved. The current and voltage was extracted from the Silvaco Software and analysis was conducted followed with plotting of the I-V graph. The results were plotted using syntax Tonyplot.

Analyses and Discussion

The influence of composition on green density was quite significant as presented in Fig. 5. The maximum value was obtained with sample I for the composition of 0.5% SiO₂, 0.5% Ta₂O₅, 0.25% WO₃ and 0.5% Bi₂O₃. Variation of atomic size resulted in better packing for this composition. The addition of SiO₂ improved the density of the sample as atomic size of Si is small which is 117.6 pm compared to Ti (176 pm) (Zainal, 2012). Therefore, the inter-particle space was occupied resulting in higher green density.

The variation of fired density for all compositions is given in Fig. 6. The highest fired density was also achieved with sample I when fired at 1400°C. It was also found that the fired density at 1400°C was higher compared to the samples sintered at sintering temperature of 1300 and 1350°C. Moreover, high temperature is necessary to promote grain growth as this combination contains the grain enhancer additives Bi₂O₃ that provide medium for liquid phase sintering (Bomio *et al.*, 2004; Zainal, 2012; Nahm, 2013; Ashraf *et al.*, 2011; El-Meliegy *et al.*, 2004; Abdullah *et al.*, 2012a; Nahm, 2014). Besides that, similar to green density the addition of SiO₂ aids to increase the density. The vacancies created by SiO₂ are responsible for the diffusion of material during sintering. It was also observed by other researchers that the addition of SiO₂ increased the density of the material (Deshpande and Deshpande, 2009).

On the other hand, the addition of 0.25% WO₃ increases the number of electrons by substituting Ti in the crystal structure which leads to the formation of solid solution. The vacancies caused by TiO₂ are filled in with WO₃ as presented by:

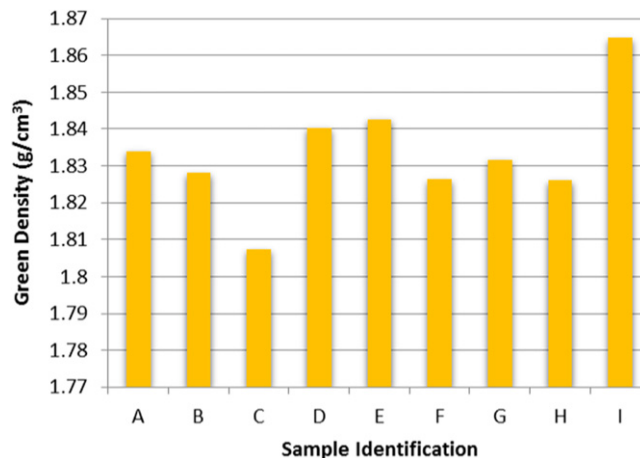


Fig. 5 Green density of samples under different compositions of TiO₂.

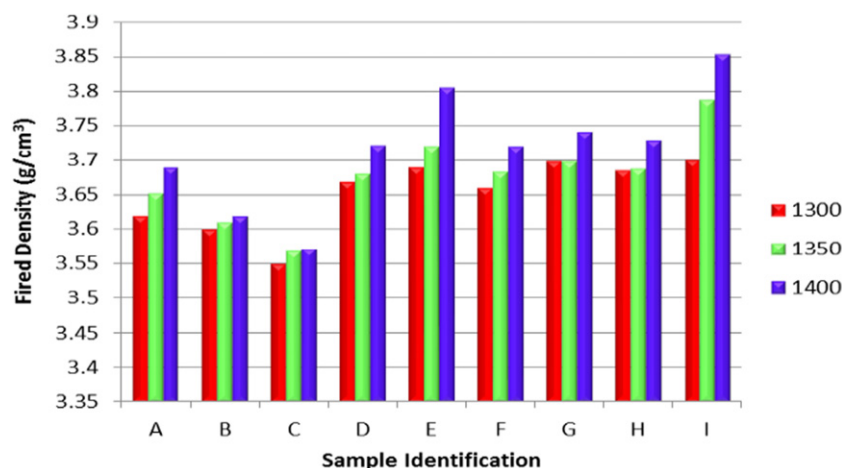


Fig. 6 Variation of fired density at different sintering temperature with the variation of composition of TiO₂.

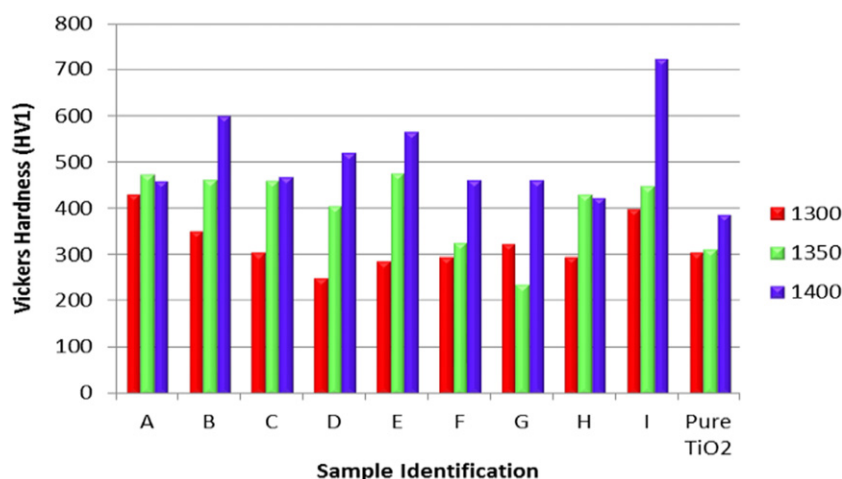


Fig. 7 Effect of sintering temperature on the Vickers hardness with the variation of composition of TiO₂.

The fired density is 3.857 g/cm³ for the pure TiO₂ varistor material (Kothandapani *et al.*, 2012; Hua, 2012). The fired density obtained with the new composition was in the range of 3.5–3.9 g/cm³. This indicates that with the new composition, improved density could be achieved.

The effect of sintering temperature on the Vickers hardness for various compositions is illustrated in Fig. 7. It can be noted from the graph that the composition sintered at 1400°C exhibited superior hardness when compared to the result obtained at 1300°C and 1350°C. It was also observed that the addition of dopants was beneficial in enhancing the hardness of TiO₂ when sintered at high temperature.

As can be observed from the Fig. 7, the hardness of TiO₂ had a maximum value for sample I when sintered at 1400°C. This coincides with the fired density where the highest fired density was achieved for Group I when sintered at 1400°C. The addition of dopants also improved the mechanical strength for the new composition when compared to pure TiO₂ as delineated in Fig. 8. This is because dopants aid in filling up the pores of the sample. As doping level increases, the densification was accelerated, and grain growth mobility is evident. Besides that, the dopants fill in the voids in the TiO₂ material. The addition of WO₃ improves the density of TiO₂ varistor and reduces defects (Sayuti, 2012). Moreover, silicon has high hardness and a low specific gravity which attributes to higher strength and hardness (Ming *et al.*, 2011). Not only that, the addition of WO₃ and Ta₂O₅ plays an important role that could trigger a mechanism because of its high melting point. This observation indicates the transformability of the cubic grains of TiO₂ that are more dependent on the WO₃ than Ta₂O₅ concentration (Hua *et al.*, 2011; Sousa *et al.*, 2002).

The average grain sizes were determined from the microstructure evaluated by scanning electron micrograph and presented in Table 3. The results of Table 3 signify the importance of dopants when compared to undoped TiO₂ sintered at the same sintering temperature as shown in Figs. 9–14. The SEM indicates that larger average grain size can be found in Group 16, 17, 18, 26 and 27. It is evident that the grain size increases when sintering temperature is high (1400°C). The high sintering temperature promotes the

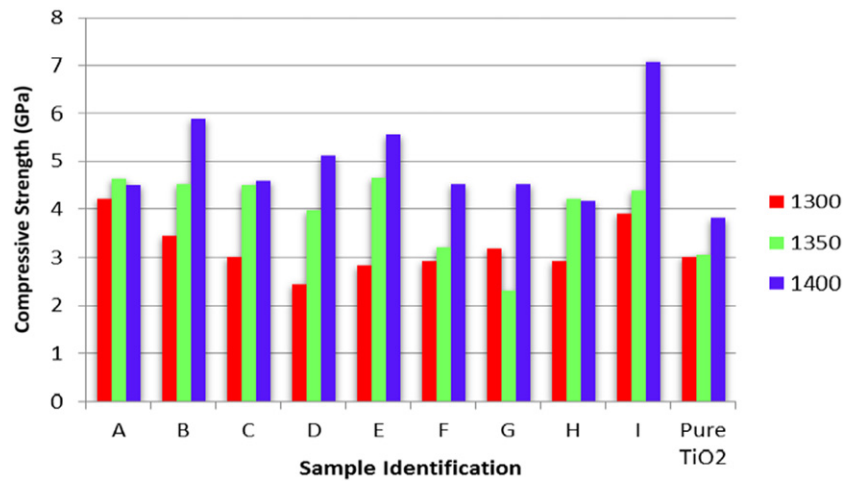


Fig. 8 Effect of sintering temperature on the compressive strength with the variation of composition of TiO₂.

Table 3 Average grain size (μm) of TiO₂ based varistor samples sintered at different sintering temperature with various dopants

Experiment	SiO ₂ (wt%)	Ta ₂ O ₅ (wt%)	WO ₃ (wt%)	Bi ₂ O ₃ (wt%)	Sintering temperature (°C)	Average grain size (μm)
2	0.3	0	0.25	0.5	1300	0.28
3	0.5	0	0.25	0.5	1300	0.74
4	0.1	0	0.25	0.5	1400	1
8	0.5	0	0.25	0.5	1400	1.08
11	0.3	0.25	0.25	0.5	1300	0.83
16	0.1	0.25	0.25	0.5	1400	1.49
17	0.3	0.25	0.25	0.5	1400	1.15
18	0.5	0.25	0.25	0.5	1400	1.67
26	0.3	0.5	0.25	0.5	1400	1.25
27	0.5	0.5	0.25	0.5	1400	1.65

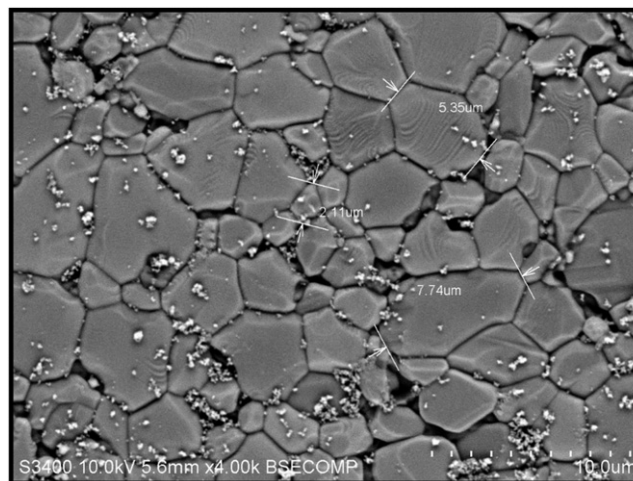


Fig. 9 SEM micrograph for undoped TiO₂ at 1400°C.

transport of ions which facilitates the grain growth accordingly. The largest average grain size was found in Experiment 18 where 0.5% SiO₂ and 0.25% Ta₂O₅ was added.

It was observed that there was a decrease in grain size when more Ta₂O₅ was added as shown in Fig. 14. This observation indicates that an adequate amount of Ta₂O₅ has strong influence on the average grain size of TiO₂ at high sintering temperature. Large amounts of Ta₂O₅ caused segregation and decreased the grain boundary mobility (Bastami and Nassaj, 2012; Castro and

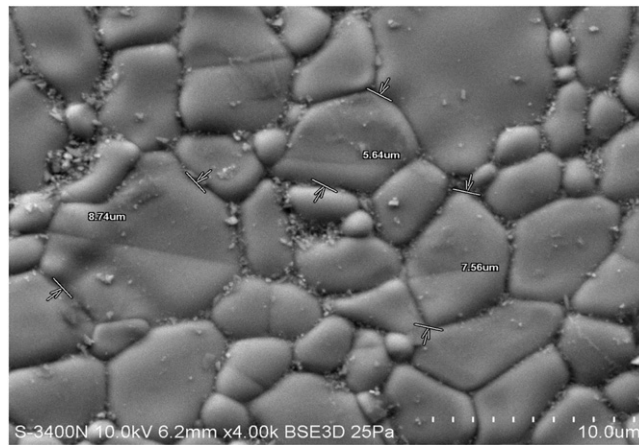


Fig. 10 Scanning electron microscopy image for experiment 16 (0.1% SiO_2 , 0.25% Ta_2O_5 , 0.25% WO_3 and 0.5% Bi_2O_3 sintered at 1400°C).

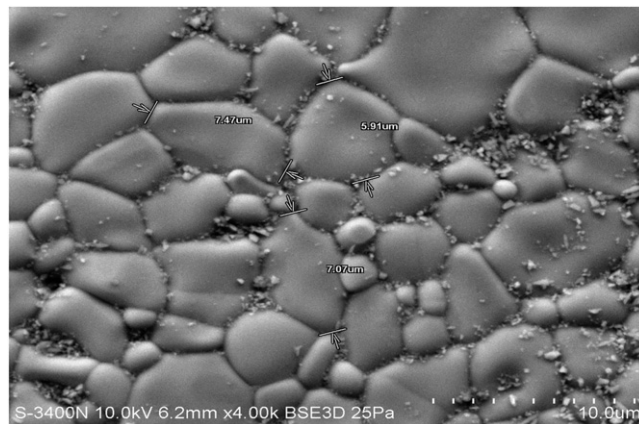


Fig. 11 Scanning electron microscopy image for experiment 17 (0.3% SiO_2 , 0.25% Ta_2O_5 , 0.25% WO_3 and 0.5% Bi_2O_3 sintered at 1400°C).

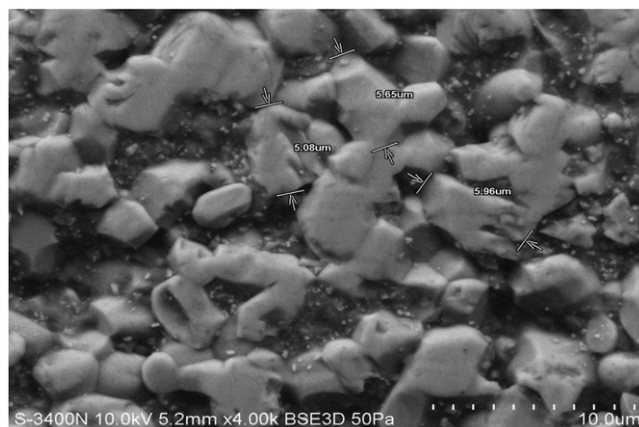


Fig. 12 Scanning electron microscopy image for experiment 18 (0.5% SiO_2 , 0.25% Ta_2O_5 , 0.25% WO_3 and 0.5% Bi_2O_3 sintered at 1400°C).

Aldao, 1999), thereby, decreasing the average grain size of the sample. Grain growth is also achieved when doped with WO_3 since its radius is similar to Ti which will lead to the formation of solid solution with TiO_2 lattice. It is well established that addition of Bi_2O_3 into the system produces an increase in grain growth because of the formation of liquid phase which results in grain rearrangements and mass transfer (Qian *et al.*, 2013).

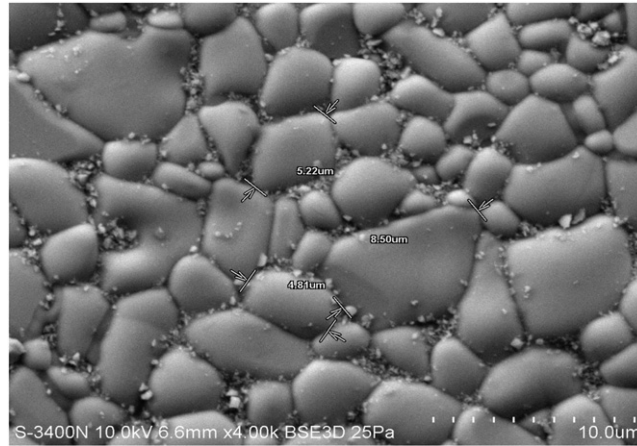


Fig. 13 Scanning electron microscopy image for experiment 26 (0.3% SiO_2 , 0.5% Ta_2O_5 , 0.25% WO_3 and 0.5% Bi_2O_3 sintered at 1400°C).

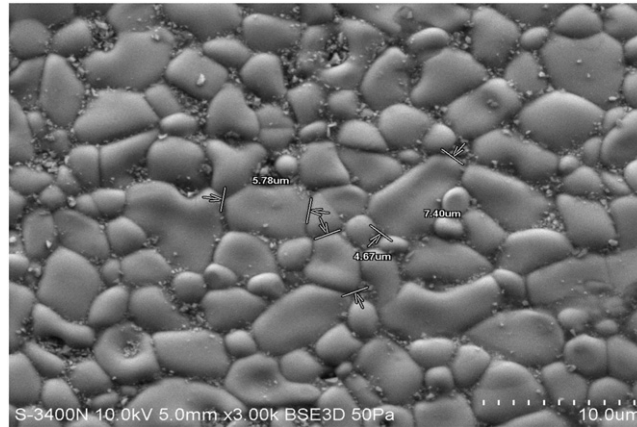


Fig. 14 Scanning electron microscopy image for experiment 27 (0.5% SiO_2 , 0.5% Ta_2O_5 , 0.25% WO_3 and 0.5% Bi_2O_3 sintered at 1400°C).

Table 4 Breakdown voltage of TiO_2 varistor samples sintered at different temperatures with various dopants

Experiment	SiO_2 (wt%)	Ta_2O_5 (wt%)	WO_3 (wt%)	Bi_2O_3 (wt%)	Sintering temperature ($^\circ\text{C}$)	Breakdown voltage (mV/mm)
2	0.3	0	0.25	0.5	1300	5607.14
3	0.5	0	0.25	0.5	1300	1945.95
4	0.1	0	0.25	0.5	1400	1870.37
8	0.5	0	0.25	0.5	1400	1570
11	0.3	0.25	0.25	0.5	1300	1951.81
16	0.1	0.25	0.25	0.5	1400	1504
17	0.3	0.25	0.25	0.5	1400	1462.96
18	0.5	0.25	0.25	0.5	1400	910
26	0.3	0.5	0.25	0.5	1400	1365.22
27	0.5	0.5	0.25	0.5	1400	1093.96

Table 4 shows the breakdown voltage of samples for which SEM was carried out. It can be seen from **Table 4**, the breakdown voltage for this varistor material is low which is suitable for low voltage application. From **Table 4**, in Experiment 18, the largest average grain size leads to the lowest breakdown voltage. The high sintering temperature causes grain growth, and this leads to the decrease in grain boundaries owing to the large grain size. Therefore, low breakdown voltage was found in the grain boundaries. Moreover, at high sintering temperature, large ionic radius of bismuth segregates in the grain boundaries which aids in increasing the grain growth. The addition of tantalum can lead to the increase or decrease of the grain conductivity depending on the donor compensation (Navale *et al.*, 2007). However, 0.5% Ta_2O_5 results also in small

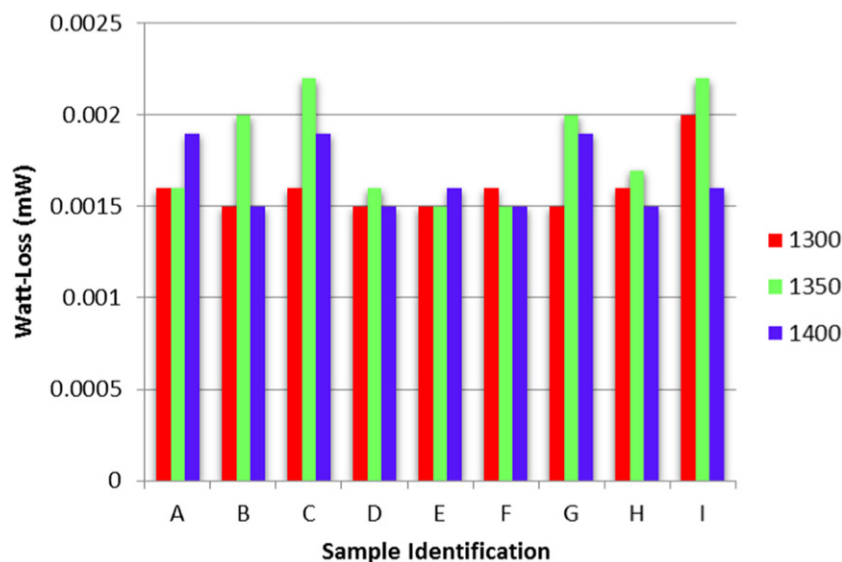


Fig. 15 Watt-loss behavior of TiO₂ based varistor material at different sintering temperature for various compositions.

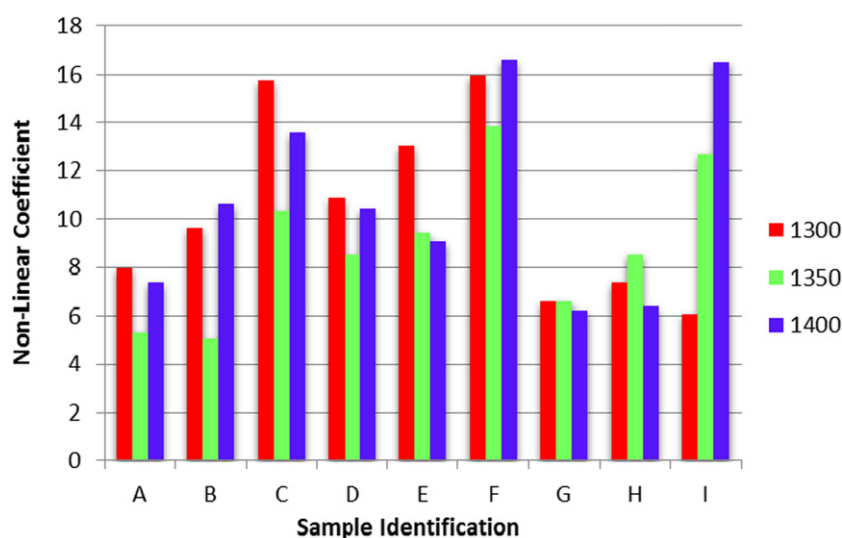


Fig. 16 Nonlinear coefficient variation of doped samples sintered at different temperatures.

breakdown voltage, though it is a bit larger when compared to 0.25% Ta₂O₅ because the donors are compensated with cation vacancies which lead to higher resistivity.

The effect of dopants and sintering temperature on watt-loss is presented in Fig. 15. It is evident that the watt-loss for all the experiments does not differ much. The range of watt-loss is from 0.0015 to 0.0022 mW which is considerably small for all the samples. Minimum watt-loss was obtained for various compositions when sintered at 1400°C. Low watt-loss indicates higher reliability against degradation under normal operation.

The non-linear coefficient of samples for various compositions under different sintering temperature is delineated in Fig. 16. Significantly high non-linear coefficient (α) of value 16.5 was obtained at sintering temperature 1400°C with the samples having the composition of 0.5% SiO₂, 0.25% Ta₂O₅, 0.25% WO₃ and 0.5% Bi₂O₃. The sintering temperature can affect the conductivity of the material. The higher sintering temperature leads to faster conductivity as the tightly bonded valence electrons can only conduct electrical current when they are highly energized (Castro and Aldao, 1999).

From Fig. 16, it can be observed that at the same sintering temperature, the non-linearity is decreased with the increase of Ta₂O₅ doping level after a certain limit. As an agreement with the previous researchers (Yaya and Dodoo-Arhin, 2012; Luo *et al.*, 2008; Filho *et al.*, 2004), improvement in electrical properties of semiconductor is defined by free charge electrons that moved by applying an external force and is responsible for conduction. An addition of Ta₂O₅ that consist of five valance

electrons can form solid solution with four neighboring atoms of Ti⁴⁺ due to its ionic radius similarity which are 0.064 and 0.061 nm, respectively, thus leave an extra electrons that move and increase the conductivity of varistor (Su *et al.*, 2005). However, the non-linear coefficient reduces when Ta₂O₅ concentration is 0.5%. This is because of the increase in width of depletion layer which prevents the tunneling of electrons. Hence, this results to lower down the electrical conductivity (Filho *et al.*, 2004; Nahm, 2008).

The ionic radius of W³⁺ is larger than Ti⁴⁺, thus, when W³⁺ ion is replaced in TiO₂ lattice, there will be liberation of net electron to the conduction band and will promote the formation of positive charge that later alter the electronic state at grain boundary. This phenomenon resulted in an increase of non-linearity of TiO₂. Such observation has been reported by Dhage *et al.* (2007) and Navinsek and Carte (1968) in their work to confirm the relationship between the trivalent ions with the non-linearity of varistor material. Besides that, from Fig. 16, it could be seen that the non-linear coefficient also increases when the SiO₂ concentration is high (0.5%). SiO₂ facilitates grain growth at the grain boundaries. This is evident in Experiment 18 and 27.

The effect of dopants and sintering temperature on the clamping ratio of TiO₂ is shown in Fig. 17. Overall clamping ratio is low. The lowest value of 1.05 was achieved with Group F. This coincides with the non-linear coefficient where α was highest in Group F at sintering temperature 14000°C. In Group I, low clamping ratio was also achieved. Low clamping ratio is achieved because Ta₂O₅ is present at the grain boundaries during high sintering temperature which decreases grain resistivity.

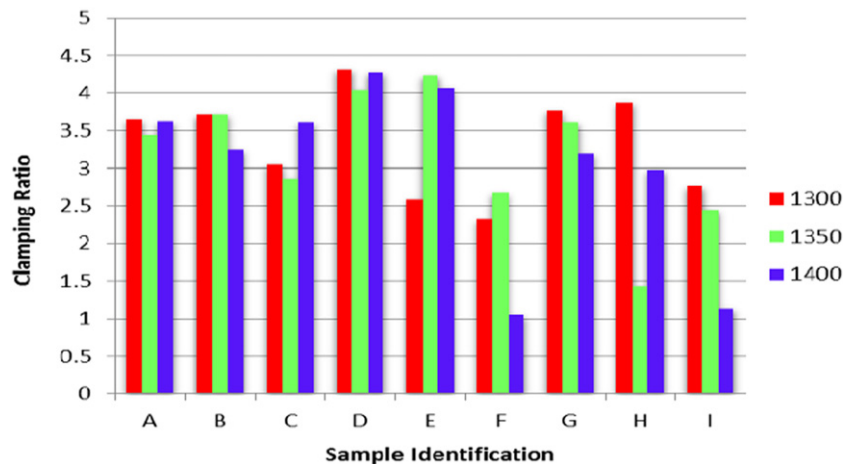


Fig. 17 Variation of clamping ratio for different composition of TiO₂ sintered at various temperatures.

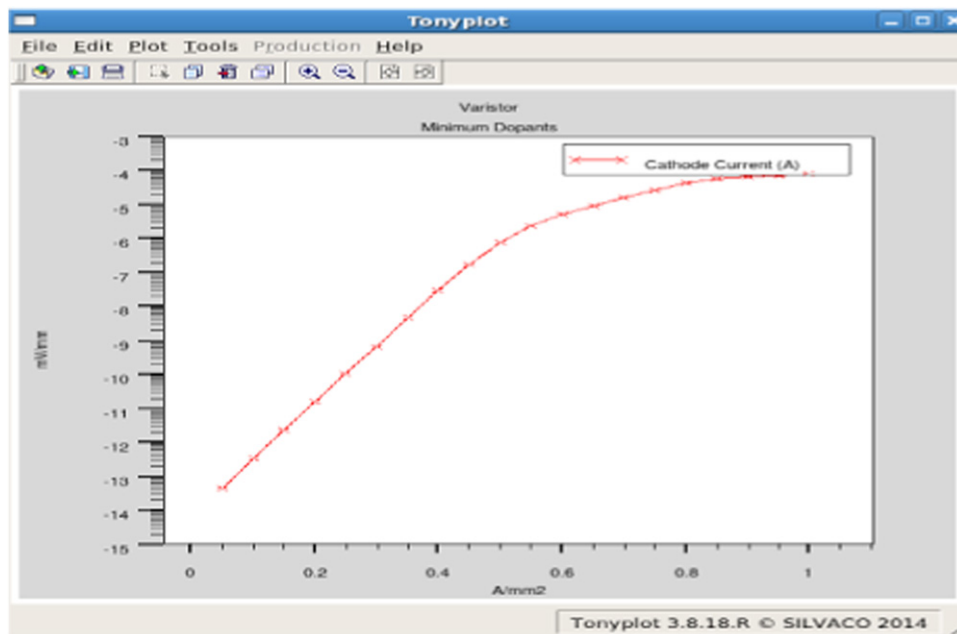


Fig. 18 Simulation result for minimum level of dopants.

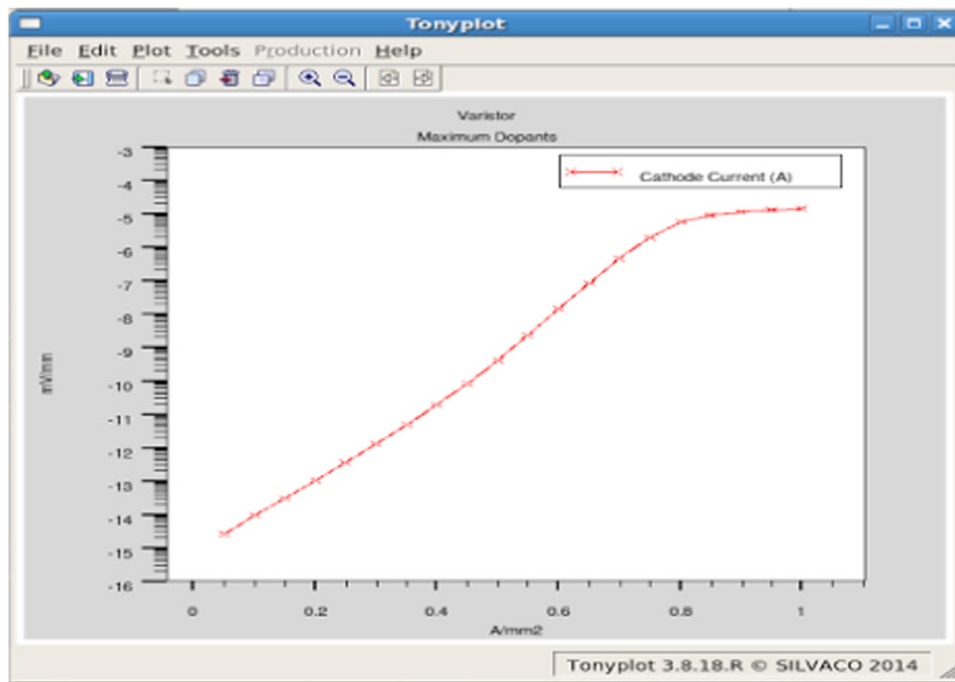


Fig. 19 Simulation result for maximum level of dopants.

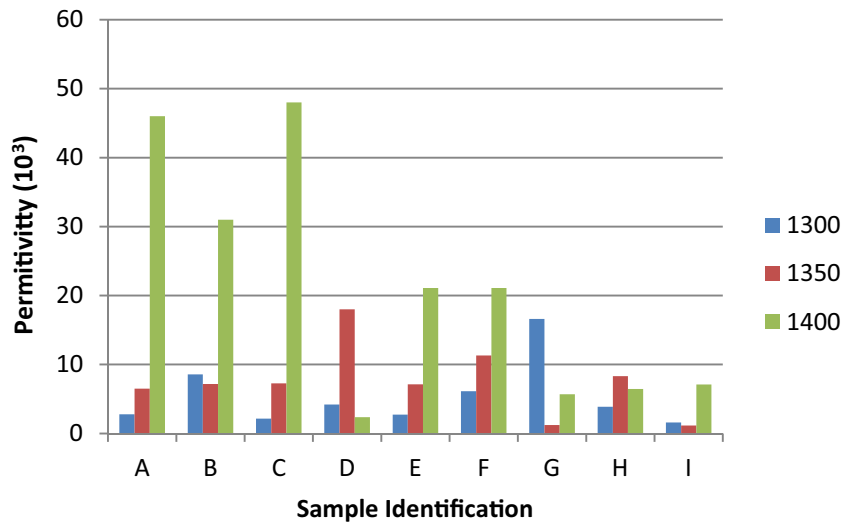


Fig. 20 Influence of sintering temperature on permittivity of doped TiO₂ at 100 Hz.

The experimental non-linear value was also verified by simulation, where various compositions were considered. In Fig. 18, the I-V curve with minimum concentration for dopants SiO₂ and Ta₂O₅ was considered. The composition was consisted of TiO₂ = 1.0, SiO₂ = 0.001, WO₃ = 0.0025, Ta₂O₅ = 0 and Bi₂O₃ = 0.005. On the other hand, Fig. 19 depicts the I-V curve with the composition of TiO₂ = 1.0, SiO₂ = 0.005, WO₃ = 0.0025, Ta₂O₅ = 0.005 and Bi₂O₃ = 0.005, where the maximum concentration of SiO₂ and Ta₂O₅ was considered.

From Fig. 16, it can be seen that the nonlinear coefficient ranges between 5.5 and 16.5. However, the simulation provided higher value of nonlinear coefficients which are within the range of 7.7–21.4. The percentage difference between the results in Silvaco and experimental is 25%. The difference in results is most probably caused by contamination during experiment.

The effect of Ta₂O₅ and WO₃ on permittivity of the TiO₂ varistor is shown in Fig. 20. The highest permittivity achieved was 4.89×10^4 at 100 Hz with sample C when sintered at 1400°C and measured at 100 Hz. The permittivity of the test material ranged from 2.78×10^3 to 4.89×10^4 . The new composition of varistor material resulted in very high permittivity at higher sintering temperature.

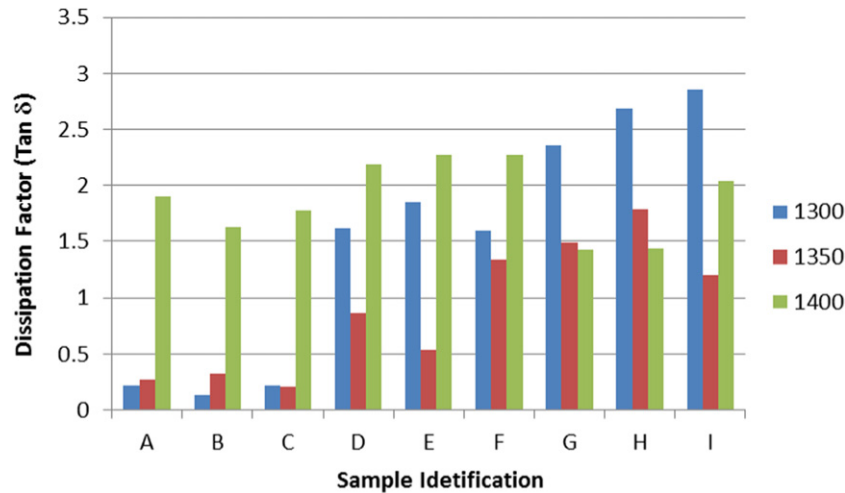


Fig. 21 Dissipation Factor (Tan δ) of doped samples sintered under different sintering temperature.

The high permittivity is resulted due to the less resistivity of TiO₂ grains than that of the grain boundary layers. Thus the entire voltage is sustained across narrow intergranular regions and the polarization is large. The relative permittivity gradually decreases as the frequency increases. Besides that, the addition of SiO₂ also aids in increasing the permittivity as it facilitates grain growth.

The dissipation factor (Tan δ) of all doped samples when sintered at 1300–1400°C is shown in Fig. 21. For different compositions under different sintering temperature, it does not show any particular trend. The minimum value of dissipation is 0.219 for the composition of 0.0 wt% of Ta₂O₅ + 0.25 wt% of WO₃ + 0.30 wt% of SiO₂ + 0.50 wt% of Bi₂O₃ when sintered at 1300°C and measured at 100 Hz. The highest value of dissipation factor of 2.86 was achieved for composition of 0.5 wt% of Ta₂O₅ + 0.25 wt% of WO₃ + 0.50 wt% of SiO₂ + 0.50 wt% of Bi₂O₃ when sintered at 1300°C. For the same composition the value was much lower when sintered at 1400°C. This result indicates that the dissipation factor (Tan δ) decreases with the increase of dopants level and sintering temperature due to the decrease in joule heating loss by leakage current and frictional heating loss by electric dipole rotation (Epstein, 1995).

Conclusions

The physical and mechanical properties, microstructure and electrical performance of low voltage titanium oxide based varistor material are significantly improved by using multiple dopants and by the variation of sintering temperature. The sintered properties of the varistor disks were improved with the use of multiple dopants and variation of sintering temperature. The effect on physical and mechanical properties and microstructure were found to be translated into the electrical performance of the disks. Low breakdown voltage, low watt-loss and clamp ratio, and significantly high non-linear coefficient with high consistency were secured. The permittivity achieved with the new composition was also significantly high. Low value of dissipation factor indicated less leakage current under normal operation. It was found that for any compositions sintering temperature of 1400°C is highly recommendable for TiO₂ based low voltage varistor. The simulation result also exhibited the same trend. Hence based on the analysis it can be concluded that the composition of 0.5 wt% SiO₂ + 0.5 wt% Ta₂O₅ + 0.25 wt% of WO₃ + 0.5 wt% Bi₂O₃ at 1400°C would generate low voltage TiO₂ based varistor with requisite properties.

Acknowledgments

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A Review of TiO₂-nanoparticle Reinforced Lead-Free Solder Composites Used in Electronic Components Soldering

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Abstract

Lead-free solder alloys have become popular and largely adopted as an alternative to lead-based solder alloys in the soldering of electronic components and electronic packaging. Ever since the legislation on end-of-life disposal and the European Union's (EU) Restriction of Hazardous Substances (RoHS) directive has led to the elimination of lead-based solder and made Sn-Ag-Cu eutectic and Sn-Cu eutectic acceptable alternative. However, researchers continue their endeavor to find more reliable and less expensive alternatives. Recently, several additives prove to enhance the solder properties and these composites are capturing attention especially for Sn-based lead-free solder. The addition of nanoparticles into Sn-based solder alloys improves the solder joint strength, refine the intermetallic compound (IMC), suppresses the IMC growth, and increases the matrix strength and joint reliability. Several other superior attributes can be achieved by adding nanoparticles into solder alloys. This paper particularly reviews the effect of TiO₂ nanoparticles on a lead-free Sn-based solder system.

Key Terms

Intermetallic Compounds: Intermetallic compounds are solid phases that involve two or even more metallic elements or semi-metallic elements having an ordered structure.

Solder: Solder is a metallic material that is usually used for metal workpieces connection.

Introduction

Solder alloys are used as filler metal during soldering. Soldering is a metallurgical joining technique used for joining electronic components. Sn-Pb solder alloys were widely used in electronic packaging industries (Aamir and Muhammad, 2020). Lead is a toxic element, thus it has many adverse effects on mankind and the environment. To mitigate the adverse effects of lead, lead-free solder alloys are used in electronic industries. To avoid the use of lead-based solder alloys, Sn-based solder alloys such as Sn-Ag-Cu, Sn-Zn, Sn-Bi, Sn-Cu-Ni, and Sn-Cu have been produced (Ohguchi and Sasaki, 2011; Shen *et al.*, 2014; Ramos *et al.*, 2020; Silva *et al.*, 2015; Yen *et al.*, 2019). However, solder properties, mechanical and reliability properties of the solder joint, costs, and regulations relevant issues are associated with these Sn-based solder alloys, such as high soldering temperature, poor reliability, poor wettability, and high price. The advantages and disadvantages of lead-free Sn-based solder systems are listed in Table 1.

The efficiency of these lead-free solder alloys can be improved by nanoparticle strengthening (Zhang *et al.*, 2019). The melting temperature of lead-free solder alloys is higher than the lead-based solder alloys (Ghaleeh *et al.*, 2020; Liu *et al.*, 2020). Therefore, lead-free solder alloys with higher soldering temperature create defects at the solder joint. Forming a composite by adding nanoparticles is an effective way of producing a new solder alloy having a low melting temperature. Besides, nanoparticle addition can also improve other mechanical, electrical, and chemical properties (Chen *et al.*, 2010). It was found that nanoparticle reinforced solder composites show better creep resistance than eutectic and near eutectic solder alloys. Creep-rupture life improves with increasing the amount of nanoparticles up to a certain point and then decreases with a further addition of nanoparticles (Shi *et al.*, 2008). One of the objectives of designing composites is to enhance the creep and fatigue resistance of solder alloys. This can be achieved by distributing the nanoparticles or reinforcements inside the grains as well as at the grain boundaries. These second phase particles hinder the dislocation motions and sliding of grain boundaries (GB) at high service temperature (Shen and Chan, 2009). During soldering, intermetallic phases are formed at the solid/liquid interface. The reliability of solder joints during service periods primarily depends on intermetallic compounds (IMC) formed at the interface (Zhang and He, 2013). A thin IMC layer improves the wettability of solder alloys. However, these IMCs are brittle, and thick IMC layers weaken the solder joint (Tan *et al.*, 2015). TiO₂ nanoparticles restrain the IMC growth and produce fine intermetallic compounds (Tsao *et al.*, 2016; Huang *et al.*, 2015). In this review article, the effects of TiO₂ nanoparticles addition into different lead-free Sn-based solder systems are discussed. TiO₂-nanoparticles addition affects mostly the microstructure, mechanical properties, IMC layer, melting temperature, and wettability of the solder systems.

Influence of TiO₂ Nanoparticle Addition into Different Solder Systems

TiO₂ incorporation affects the properties of the solder system. The influence of TiO₂ on microstructure, hardness, IMC layer, joint strength, and wettability are discussed in the following sections.

Table 1 Advantages and disadvantages of some lead-free Sn-based solder systems

Solder Alloys	Advantages	Disadvantages	References
Sn-Pb	-Stable microstructure -Excellent wettability -Melting temperature is ideal	-These solder alloys are toxic -Sensitive to the concentration of Sn	(Sonwane and Raja, 2019; Mohd <i>et al.</i> , 2006; Moosakazemi <i>et al.</i> , 2020)
Sn-Zn	-Low cost -IMCs don't form during equilibrium -Better ductility -Appreciable shear and tensile strength	-These alloys are corrosive -Atmospheric corrosion occurs -Liquid phase is formed at 199°C -Poor wetting -Oxidation problem	(Efzan <i>et al.</i> , 2013; El-Daly and Hammad, 2010; Osório <i>et al.</i> , 2013)
Sn-Ag-Cu(SAC)	-Steady creep rate -Strength, as well as ductility, of the solder joint is relatively better	-High cost -Formation of voids in solder joints -High stiffness -Higher melting point	(Aamir and Muhammad, 2020; Liu and Lee, 2007)
Sn-Cu(SC)	-SC solder alloys are less costly than SAC solder alloys -Good solder-ability -High strength -Wear resistance -Low melting temperature	-Cu dissolution -Low mechanical strength and reliability	(Nasir <i>et al.</i> , 2016; Osório <i>et al.</i> , 2011; Bogno <i>et al.</i> , 2015; Zhao <i>et al.</i> , 2019)

Microstructure and Hardness

Sn-Ag-Cu (SAC) lead-free solder system is a leading contender to replace lead-based (Pb-Sn) solder alloys on account of their excellent mechanical properties compared to Pb-Sn solder alloys. Yet, Pb-Sn solder alloys possess better wettability than SAC solder systems. Another important issue to mention is that high Ag contentment in SAC solder provokes Ag₃Sn formation. Ag₃Sn phase is brittle in nature (Zhao *et al.*, 2020). Sonwane *et al.* observed a correlation between Sn content and void formation. They found that with the increment of Sn content, the probability of void formation and large undercooling during solidification increases (Sonwane and Raja, 2019). They also claimed that the brittle nature of SAC solder alloys was due to its high stiffness and excessive reactions at the solder interface. It has been reported that Ag content should be less than 0.25 wt% in order to improve shock performance, where Cu content should be between 0.75.75 wt% and 1.0 wt%. Yunus *et al.* (2003) worked on the effects of these void formations and found voids having an area larger than 50% of solder joint reduce the joint-life by 25%–50% during mechanical testing. Thus, the product's potential reliability is reduced. The reliability of the solder joint depends upon the voids volume fraction, the location, and voids distribution. The fatigue life of solder joints decreases with increasing the void percentage. The phenomenon of void diffusion also plays a salient role in solder degradation (Le *et al.*, 2016). The role of TiO₂ nanoparticle incorporation into SAC solder systems has drawn interest to research community in order to suppresses the formation of voids in solder joint (Cheani *et al.*, 2018a). Tsao (2011) in his classical work closely observed the morphological change when an incremental amount of TiO₂-nanoparticles was added to SAC solder alloys. He found that when 1 wt% and 1.25 wt% of TiO₂ nanoparticles were added into the SAC solder alloy, micro-pores were formed along the grain boundary (Fig. 1). The microstructure of high resolution of a solder composite which was reinforced by 1 wt% of TiO₂ particles is shown in Fig. 2. The black spots in the microstructure resemble the presence of micro-pores. Tsao and Chang reported the same statement about the micro-porosity in another work (Tsao and Chang, 2010). They observed micro-porosity at the eutectic network when 1 wt% TiO₂ nanoparticles were added. It is, therefore, can be concluded based on the stated research work that a large amount of TiO₂ nanoparticles causes microstructural irregularities, and micro void formation is a typical effect of it.

Solder joints with TiO₂ nanoparticles exhibit a persistently higher hardness value than the plain SAC solder joints in every new reflow cycle. The hardness value of the bulk solder is enhanced due to the homogeneous dispersion of TiO₂ nanoparticles and well-managed finer Intermetallic Compound particles (Kumar *et al.*, 2011). Nasir *et al.* (2015) studied the effect of TiO₂ nanoparticles addition on hardness. They found the hardness of SAC107 solder alloy 13.58HV. Due to the incremental addition of TiO₂-nanoparticles, i.e., 0.25%, 0.5%, 0.75%, 1.0%, the hardness increases to 14.68, 15.26, 15.6, and 15.76HV, respectively. Yahaya *et al.* (2016) in their work incorporated various amounts of TiO₂ nanoparticles into SAC305 solder alloy to examine the composite hardness. They measured a hardness value of 1.78 GPa when 1 wt% TiO₂ was added into the alloy. Fine Cu₆Sn₅ and Ag₃Sn Intermetallic Compounds are produced due to the addition of TiO₂ into SAC305–1.0TiO₂. These fine phases act as a barrier to dislocation motions. The hardness of SAC305–1.0TiO₂ increases because of such resistance to dislocation motions. However, a reverse trend, decrease of hardness value to 1.68 GPa, was observed when the TiO₂ content is increased to 1.5 wt%. Yahaya *et al.* (2020) noticed an appearance of TiO₂ at solder interface, which causes the suppression of growth of Cu₆Sn₅ layer. They also claimed that the incorporation 1 wt% TiO₂-nanoparticles eliminates thick Cu₆Sn₅ at the morphology. As a result, the area of indentation and

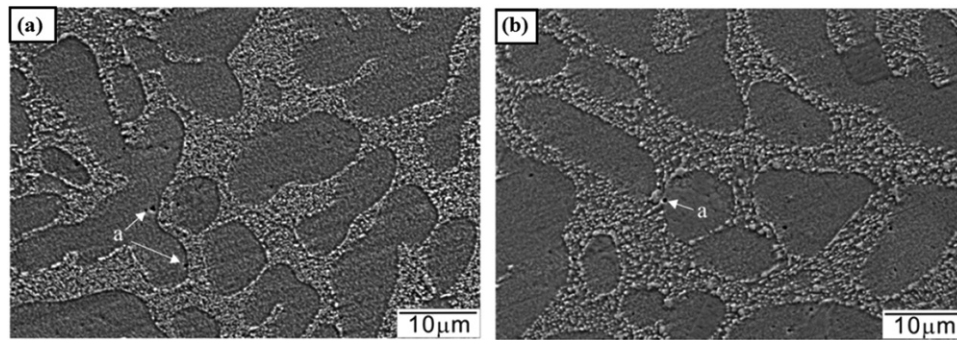


Fig. 1 SEM image of Sn-Ag-Cu solder alloy with various wt% TiO₂ nanoparticles, solidified at the condition of rapid cooling: (a) SAC-1 wt% TiO₂; (b) SAC-1.2 wt% TiO₂. Reproduced from Tsao, L.C., 2011. An investigation of microstructure and mechanical properties of novel Sn3. 5Ag0. 5Cu – X TiO₂ composite solders as functions of alloy composition and cooling rate. *Materials Science & Engineering A* 529, 41–48. Available at: <https://doi.org/10.1016/j.msea.2011.08.053>.

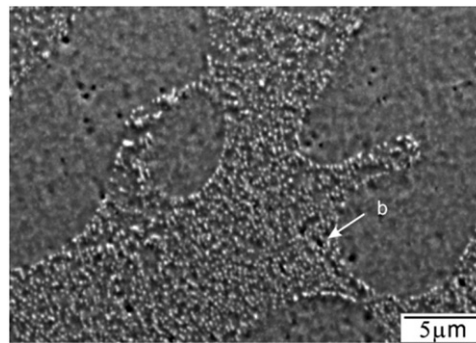


Fig. 2 SEM image of Sn-Ag-Cu-1 wt%TiO₂ solder composite. Reproduced from Tsao, L.C., 2011. An investigation of microstructure and mechanical properties of novel Sn3. 5Ag0. 5Cu – X TiO₂ composite solders as functions of alloy composition and cooling rate. *Materials Science & Engineering A* 529, 41–48. Available at: <https://doi.org/10.1016/j.msea.2011.08.053>.

depth are decreased when TiO₂ is added at 1 wt%, and thus leads in obtaining the hardness of optimum value. Nasir *et al.*, added TiO₂-nanoparticles into SAC305 solder alloys and examined the microstructure of the solder/substrate interface. They observed the interface of SAC305–0.1TiO₂ and found the presence of dot-shaped Ag₃Sn which exists at the interface of SAC305 solder alloys. They also reported that the existence of TiO₂ nanoparticles reduces the size of Cu₆Sn₅ phase. The refined Cu₆Sn₅ phase, as well as Ag₃Sn phase, restrained the motion of dislocations which results in an increment of the hardness of solder joints (Nasir *et al.*, 2019). Salleh *et al.* (2015) used a microwave sintering process in order to produce TiO₂-nanoparticles incorporated SCN solder samples and claimed the process improves the hardness. Microstructure analysis of sintered products revealed that fine intermetallics ((Cu,Ni)₆Sn₅) were formed in the grains and these intermetallics were homogeneously distributed within the grains. In a similar work by Said *et al.* (2020) where they incorporated TiO₂-nanoparticles in Sn-0.7Cu-0.5Ni (SCN), and observed that the added nanoparticles acted as a heterogeneous nucleation site, and therefore fine (Cu,Ni)₆Sn₅ intermetallics were formed. TiO₂-nanoparticles incorporation in soldering alloys also decreases the surface energy of the grains, thus, the growth energy of the grains is reduced.

Intermetallic Compound (IMC) Morphology and Joint Strength

Intermetallic Compound (IMC) layer thickness and particle volume fraction are very important criteria for thermal and electrical conductivity of solder joints. Thinner the IMC layer, better the interface bonding. The addition of nanoparticles into the solder alloys refines the IMC layer by inhibiting the Cu₆Sn₅ growth, thus increase the solder joint reliability (Mukhtar *et al.*, 2019). Furthermore, the surface-active material content is increased in solder joint because of ceramic nanoparticle addition which increases the content of engrossed particles to the maximum value at the IMC surface. As a result, the IMC growth rate is decreased due to an increment in the content of engrossed material (Yakymovych *et al.*, 2016). Cheani *et al.* investigated the effect of TiO₂, added from 0 wt% to 0.05 wt%, into SAC305 solder alloy, and observed that a fall of IMC layer thickness when TiO₂ content was > 0.01 wt%. The decreasing trend of the IMC layer thickness was leveled out at around 0.05 wt% and then raised drastically with a further addition of TiO₂ (Fig. 3) (Cheani *et al.*, 2018b).

Skwarek *et al.* (2020) compared the microstructure of solder joints of SAC0307 solder alloy before and after the incorporation of the TiO₂ particles. They reported that TiO₂ particles restrained the grain growth of Sn, and as a result, the grain size was reduced

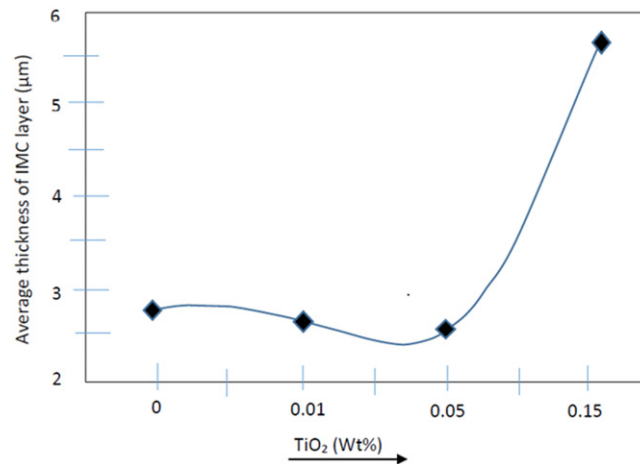


Fig. 3 Relationship between TiO₂ content and average thickness of IMC layer. Reproduced from Cheani, F., Jalar, A., Saad, A.A., *et al.*, 2018b. SAC-xTiO₂ nano-reinforced lead-free solder joint characterizations in ultra-fine package assembly. *Soldering and Surface Mount Technology* 30, 1–13. Available at: <https://doi.org/10.1108/SSMT-04-2017-0011>.

from 100 μm to around 3 μm, which indicates the refinement of grains up to 2 magnitude order. The influence of TiO₂-nanoparticle addition on IMC layer thickness is shown in **Table 2**.

In a similar study to investigate the microstructure of the composite, [Tang *et al.* \(2014\)](#) added TiO₂ nanoparticles into SAC305 solder alloys. They reported that spacing between the grains of Ag₃Sn, as well as the grain size, was decreased due to an increment in the weight percentage of TiO₂ nanoparticles addition. This trend continued up to 1 wt% of TiO₂. [Zhao *et al.*](#) proposed an equation to measure the net restraining force exerted by the entire second phase particles on grain boundary during migration, which is:

$$F_{\text{total}} = \frac{3f\gamma}{2r} \quad (1)$$

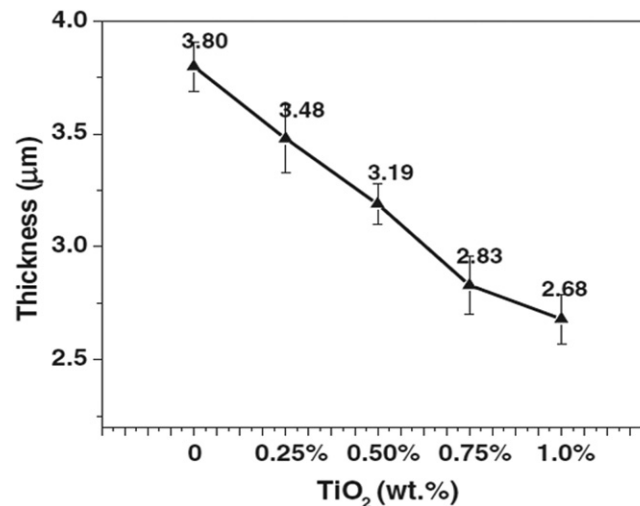
Where f is the volume fraction of second phase particle, r is the radius of second phase particles, and γ is the energy of interface per unit area at GB. From the above equation, it is evident that the tinier the second phase particle, the greater the force and the smaller the size of the grain ([Zhao *et al.*, 2016](#)). It is found that the IMC thickness of the nano-composite solder is less than the monolithic solder. [Jung *et al.* \(2018\)](#) measured the mean thickness of monolithic solder to be 3.23 μm without aging, which decreased gradually due to the addition of dual nanoparticles (TiO₂ and graphene). However, the thickness of IMC increased to 3.28 μm when nanoparticles were added in excess amount. [Cheng *et al.* \(2011\)](#) investigated various properties of the 0.5 wt% TiO₂-nanoparticles added Sn-3.5Ag and Sn-3.5Ag-0.7Cu solder alloys. They found the addition of TiO₂ nanoparticles retarded the IMC layer growth of Sn-3.5Ag-xCu ($x = 0-0.7$ wt%). The presence of TiO₂ nanoparticles produces a very fine Ag₃Sn phase. These fine Ag₃Sn phase provides dispersion strengthening as well as improves the shear strength of solder joints. The addition of TiO₂ nanoparticles also influences the contact angle and produces a contact angle of lower value, which in turn causes an increment in the shear strength ([Gill, 2015](#)). [Wen *et al.*](#) studied the size effect of TiO₂ nanoparticles on the attributes of SAC105 solder alloy. They added 6 nm and 20 nm TiO₂ nanoparticles into SAC105 solder and reported that both size ranges of the nanoparticles can impede the formation as well as the growth of the IMC layer, thus improve the joint's shear strength. However, the lower size range, which is 6 nm-sized nanoparticles, is more effective in impeding the formation and growth of the IMC layer at the time of reflowing and thermal cycling ([Wen *et al.*, 2017](#)). [Nasir *et al.* \(2016\)](#) in their work, examined the effect of 1.0 wt% TiO₂ nanoparticles addition into Sn-0.7Cu solder alloy to IMC layer and shear strength of the joint. They found that the presence of TiO₂ nanoparticles suppressed the IMC layer thickness, and as a result, IMC thickness decreased from 2.62 μm to 1.86 μm due to the addition of 1.0 wt% TiO₂ nanoparticles. They also reported an increment in shear strength due to nanoparticle addition, and shear strength increased from 8.79 MPa (Sn-0.7Cu) to 13.92 MPa (Sn-0.7Cu-1.0 T).

As a near eutectic alloy, in Sn-0.7Cu-0.05Ni system, a small amount of Cu₆Sn₅ IMCs as well as a large number of dendrites of β - Sn grain exists. The addition of TiO₂ nanoparticles refines the β - Sn grain. Atomic diffusion of Cu and Sn is blocked by the existence of TiO₂ particles. TiO₂-nanoparticles behave like the preferable sites for heterogeneous nucleation of Cu₆Sn₅ grain at the time of soldering. Besides acting as a heterogeneous nucleating site, TiO₂ particles also hinder the grain growth (**Fig. 4**) ([Ramli *et al.*, 2016](#)). When soldering is carried out, nanoparticles are finely distributed into the melted solder alloy as well as precipitated at the top of the solid surface. These regions then act like the heterogeneous nucleation areas for Cu₆Sn₅ grain. With increasing the amount of nanoparticles, the surface energy of grains (Cu₆Sn₅) decreases. As a result, grain growth velocity decreases ([Saud *et al.*, 2016](#)). At the time of isothermal aging, the existence of TiO₂ nanoparticles slows down the Cu atom diffusion rate. However, the IMC layer gets thicker for both types of solder alloys monolithic, as well as composite, when aging is performed at high temperature. This is because higher temperature provides the required thermal energy for overcoming the energy of activation for interdiffusion ([Said *et al.*, 2016](#)).

A number of researches have been so far carried out to refine the microstructural by incorporation of TiO₂ nanoparticles in various lead-free soldering alloys. [Tsao *et al.*](#) reported that the addition of a small amount of TiO₂ in the SC (Sn-Cu) solder refined the

Table 2 Influence of TiO₂ nanoparticles over IMC thickness

Solder systems	Average thickness of IMC at the bottom of the layer (μm)	References
SAC0307	2.72 ± 0.32	(Skwarek <i>et al.</i> , 2020)
SAC0307-TiO ₂	1.94 ± 0.17	
SAC0307-nanoTiO ₂	2.1 ± 0.91	
SAC305–0.01 wt%TiO ₂	2.554	(Cheani <i>et al.</i> , 2018b)
SAC305–0.015 wt%TiO ₂	1.914	
SAC-0.03% (T + Graphene)	3.17	(Jung <i>et al.</i> , 2018)
SAC-0.12% (T + Graphene)	2.68	
SAC-0.21% (T + Graphene)	2.49	
SAC-0.21% (T)	2.70	
SAC-0.6% (T + Graphene)	3.28	

**Fig. 4** Thickness of IMC layer of Sn-0.7Cu-0.5Ni as a function of TiO wt%. Reproduced from Ramli, M.I.I., *et al.*, 2016. Effect of TiO₂ additions on Sn-0.7Cu-0.05Ni lead-free composite solder. *Microelectronics Reliability* 2 –11. Available at: <https://doi.org/10.1016/j.microrel.2016.08.011>.

microstructure of composite solder. They observed that with the increase of wt% of TiO₂ nanoparticles, both the Cu₆Sn₅ IMC layer as well as β – Sn became finer. More uniform microstructures are produced due to TiO₂ nanoparticle addition, however, the eutectic colony gets thicker (Tsao *et al.*, 2012). Salleh *et al.* (2016a) in similar work, corroborated the earlier findings and reported that TiO₂ nanoparticles work as an active barrier that inhibits the growth of interfacial IMC layer at the time of soldering. Salleh *et al.* described that with the addition of 1.0 wt% TiO₂ nanoparticles into the as-flowed solder composite, the strength of the solder joints of Sn-0.7Cu is increased by approximately 20% than the mean shear strength. The joint strength of every annealed sample is improved due to TiO₂-nanoparticles addition. However, a mixture of TiO₂ nanoparticles and 0.05 wt% of Ni gives the maximum shear strength (Salleh *et al.*, 2016b). Salleh *et al.* (2016) examined the multiple reflows effect on the IMC layer and the strength of solder joint by examining the microstructure. They observed that the formed Cu₆Sn₅ crystals at the interface in Sn-0.7Cu solder alloy were needle and scalloped shaped. On the contrary, in TiO₂-nanoparticles containing solder-composite, the size and shape of Cu₆Sn₅ crystals were short and faceted. The interfacial layer thickness of Sn-0.7Cu alloy became 13 μm from 5.2 μm after multiple reflow cycles. TiO₂-nanoparticles hinder the advancement of grain growth, and thus for composites, the thickness of the layer is suppressed and the thickness was found to be 8 μm from 4.2 μm after multiple reflow cycles. Channels between Cu₆Sn₅ scallops do play an important role in interfacial Cu-Sn layer growth. TiO₂ nanoparticles which are in close contact with Cu₆Sn₅ crystals, stabilize the dissolution path of Cu and hinder the further grain growth at the time of reflow cycles. The influence of TiO₂ nanoparticles on IMC layer thickness of Sn-Cu solder systems is listed in Table 3.

Wettability

The nature of solder materials' wettability is very crucial. Solder interconnection reliability depends to some extent on wettability. Normally a smaller angle of contact indicates better wettability. The Solder-ability of a sample is examined by assessing the spreading as well as wetting property of solder on Cu substrate (Sharma *et al.*, 2015). Generally, wetting is distinguished through wetting rate and degree of wetting. The degree of wetting is indicated through the contact angle which is formed at the solid/liquid interface. The wetting rate tells us how rapidly the liquid phase wets the solid surface and layout over the surface (Prabhu, 2011). In electronics, wettability is an important factor for the formation of a bond between the substrate and the solder. The roughness of the solid surface

Table 3 Influence of TiO₂ nanoparticles on IMC layer thickness

Solder alloy	Influence of TiO ₂ nanoparticles on thickness (μm)	References
Sn-0.7Cu	2.62	(Nasir <i>et al.</i> , 2016)
Sn-0.7Cu-1.0 wt%TiO ₂	1.86	
Sn-0.7Cu	2.60	(Salleh <i>et al.</i> , 2016a)
Sn-0.7Cu-1.0 wt%TiO ₂	2.24	
Sn-Cu	2.3 ± 0.86	(Tsao <i>et al.</i> , 2012)
Sn-Cu-0.25 T	0.44 ± 0.21	
Sn-Cu-0.5 T	0.24 ± 0.06	
Sn-Cu-1.0 T	0.18 ± 0.05	

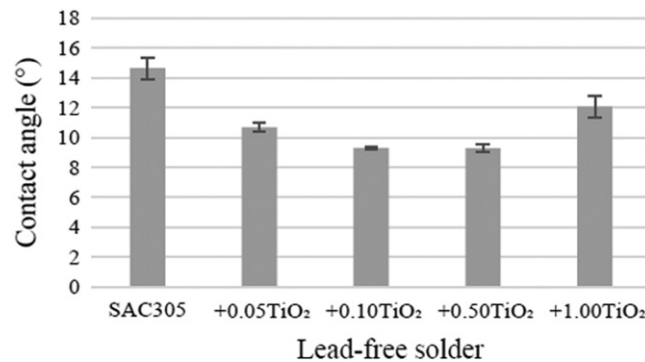


Fig. 5 Relationship between the angle of contact and wt% of TiO₂. Reproduced from Sukpimai, K., Suwannakrue, W., Kanlayasiri, K., 2019. Wettability and printability of SAC305-xTiO₂ Pb-free solder paste on Cu substrate Wettability and printability of SAC305-xTiO₂ Pb-free solder paste on Cu substrate. In: Proceedings of the IOP Conference Series Materials Science and Engineering 635. Available at: <https://doi.org/10.1088/1757-899X/635/1/012009>.

affects the capability of wetting liquid solder (Prabhu, 2012). Tsao *et al.* added TiO₂-nanoparticles into Sn-0.7Cu solder and observed its effect on wettability (Tsao *et al.*, 2010). They found the angle of contact at the equilibrium of Sn-0.7Cu solder to be 32.1° measured at 250°C with 30 min dwell time. They also observed that contact angle decreased gradually with the addition of TiO₂ nanoparticles. The contact angle was reduced to 28° from 32° when 1.0 wt% TiO₂ nanoparticles were added (Tsao *et al.*, 2010).

In a comparative study, Sukpimai *et al.* (2019) observed an optimum quantity effect of TiO₂-nanoparticles incorporation in SAC305 up to 0.5 wt% and reported a decrease of the contact angle. However, they observed a reverse trend when TiO₂ was added > 0.5 wt% (Fig. 5).

A similar decreasing trend of contact angle, thought in the wide horizon of added TiO₂-nanoparticles, was observed by Rui *et al.* (2012). They reported that with increasing the amount of TiO₂-nanoparticles, even up to 2 wt%, wetting angle decreases. Though mixed research findings were reported, there is consensus on the influence that TiO₂-nanoparticles exerts on the soldering alloy and its wettability. The surface tension of melted solder is decreased initially due to the addition of TiO₂-nanoparticle which is believed to cause the decrement of contact angle.

Conclusion

This paper reviewed the effect of TiO₂-nanoparticle addition on different Sn-based lead-free solder alloys. The melting temperature of TiO₂ is very high (1843°C), thus it remains as second phase particles in the solder matrix and improves the matrix strength. TiO₂ enhances the wettability of solder paste, improves the hardness, refines the intermetallic grains, and hinders the brittle IMC growth. Besides, TiO₂ nanoparticles not only affect the microstructure of soldered joints but also reduce the void formation in solder joints. Incorporating many good attributes into solder composites, TiO₂ nanoparticles reinforced solder composites appear as a promising alternative to lead-based solder and making their own space in the electronic industries.

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Alternative Process and Design Opportunities for ZnO-Based Surge Arrester: An Investigation Oriented Roadmap

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Abstract

The experimental findings based on several processing and operational steps are presented in this article. These experiments were related to the sintering condition, full face or partial face electroding (metallization), change in geometry from cylindrical to hexagonal, passivation thickness, fracture in high amplitude short duration (HASD) test with aluminum and steel supports, etc. The anticipated results are exploited in achieving superior performance of the arrester blocks. The characteristic feature that largely determines the functional life of a surge arrester is the energy absorption capability of each ZnO-based varistor block (disc). In the sintering process, the orientation of green arrester blocks on the sagger material regulates the defect formation for each block. The opposite flat surfaces used as contact portion of an arrester block is found to be more defect prone during sintering, and acts as the main source of failure initiation. Moreover, sintering orientation of the blocks has also dominant effect on grinding (lapping) of the flat surfaces. By arranging V-groove sintering, the scope of defect generation at the bottom surface of the block is eliminated. Thus, energy absorption capability of the disks is possible to enhance by choosing suitable orientation of the blocks during sintering. An arrester disc is usually made in the form of a cylinder having two opposite (parallel) flat surfaces. Energy from transient electrical surges or lightning strokes injected into the arrester body is transformed into heat and dissipated into the surroundings through the surface of the disc body. Heat dissipation is to be augmented by the surface to volume (S/V) ratio of an arrester block. For an arrester having hexagonal shape, the S/V ratio is increased and as a result greater energy absorption capability of a device is envisaged and verified by the experimental results. Variation of passivation thickness on the C-surface of a disc did not exhibit any significant influence on the energy absorption capability. However, the mode of failure is changed as higher passivation thickness has led to more electrical puncture rather than flashover. In the HASD current test arrester blocks fail mainly, as resembled by fracture surface, by the propagation of stress waves. Thus, the proper choice of the type of supporting material might lead to regulate failure of the disks due to shock wave. Knowledge of all these phenomena can be consolidated by choosing proper geometry of an arrester and arrester block, its sintering orientation and passivation thickness, and the support material in producing an improved arrester assembly system.

Key Term Definitions

The key term zinc oxide varistor is used for a high transient over-voltage suppressor which is fabricated from the electronic ceramic material zinc oxide. This is characterized by its excellent non-ohmic properties in current voltage relationship. The non-linear region is the heart of the device which clamps the voltage upon the application of transient surge. The flatter the non-linear region, the better the device. Addition of multiple dopants (additives) can improve the intrinsic non-linearity and reliability of zinc oxide further.

Key term energy absorption capability is the second most important parameter to judge the performance of zinc oxide varistor. The energy is calculated as J cm^{-3} , where the higher value demonstrates better energy absorption by the device from upcoming transient surge and enhanced protection for power transmission line. Grain size and its distribution and less flaws in the fired disks can improve the performance in terms of energy absorption capability.

Introduction

A ZnO varistor is a semiconducting device possessing non-linear current-voltage (*I-V*) characteristic with a symmetrical sharp breakdown similar to that of a zener diode (Matsuoka, 1971; Gupta, 1990; He, 2019). But unlike a diode, a varistor can limit over-voltages in either polarity, thus, giving rise to *I-V* characteristic which is analogous to the back to back Schottky diodes. This has enabled it to provide an excellent transient suppression performance. It is a preferred approach to protect electrical, electronic and power distribution, and transmission circuits from destructive voltage levels induced by lightning impulse or switching surges. It was introduced by Matsuoka (Matsuoka, 1971) in early 1970s, and so far it has been the most important material employed as the base for ceramic systems in the commercial production of varistors (Aguilar-Martínez *et al.*). Currently wide ranges of varistor products are available in the market (Littlefuse, 2020). The application parameters associated with various regions of the *I-V* curve are critical in design and operation of the surge protector. The product should have a low value of clamping ratio, a high value of non-linear coefficient, a low value of leakage current, high energy absorption capability leading to longer varistor life (Nahm, 2016; Begum *et al.*, 1996).

The use of ceramic as transient over-voltage protection is the development of electronic ceramics. There are two major categories of transient over-voltage suppression in the electronic power systems. One is based on the principle of attenuating the transient signals, and the other is on diverging sensitive load and thereby limiting the residual voltages. The first category suppressor is filter (capacitor) which is inserted in series within the circuits and attenuates the transient (high frequency) and allows the signal and power flow (low frequency) to continue undisturbed condition. The second type of suppressor is a crowbar type device.

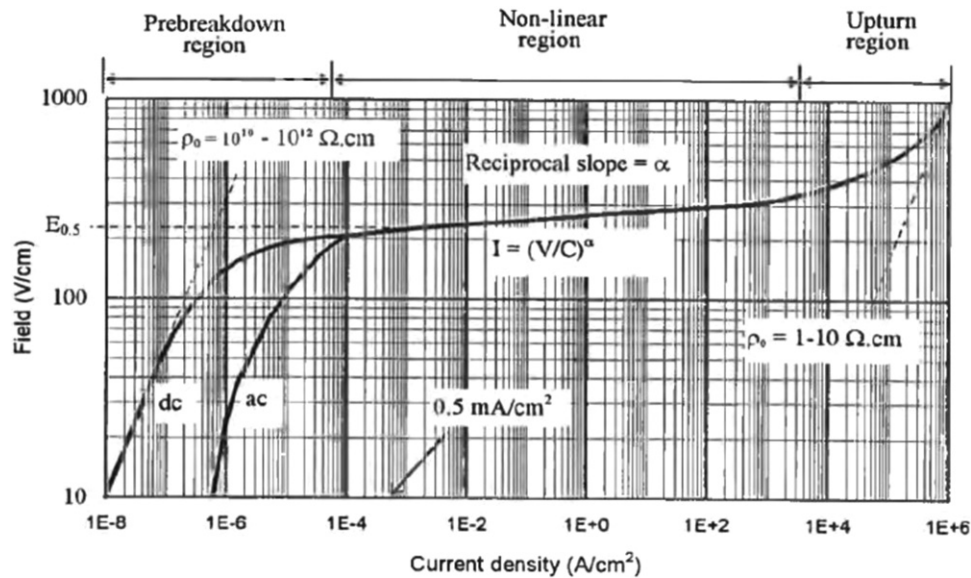


Fig. 1 Current voltage characteristics of ZnO varistor. Reproduced from Littelfuse, 2020. Metal Oxide Varistor(MOVs): Industrial High Energy Terminal Varistors. DHB34 Series. Littelfuse. https://m.littelfuse.com/~media/electronics/datasheets/varistors/littelfuse_varistor_dhb34_datasheet.pdf.

Processing of Arrester Block

Zinc oxide varistor is a high transient over-voltage suppressor. It has very large suppression capabilities, which are considered as the combination of both the feature of silicon-zener diodes and silicon carbide varistor. This device is characterized by the excellent symmetric nonlinear current-voltage behavior (Topcagica *et al.*, 2018) as shown in Fig. 1. The nonlinear feature of the ZnO varistor is attributed to the grain boundary phenomenon, and this is the intrinsic property of the ceramic material.

The high voltage application usually covers from kV to MV range for the protection of electric power distribution and transmission systems. Cylindrical disks are made to provide high energy handling capability and long term stability in stressful applications. Usually arrester disks are assembled in the Porcelain Polymeric housing “Under-oil” and Metal Clad Variety are applied for lightning protection of the electrical distribution transformer and systems. An example of a surge arrester (Amotch Co, 2003) containing several ZnO-based disks connected in series inside the assembly is illustrated in Fig. 2.

Zinc Oxide varistors produced in the form of cylindrical blocks are often called arrester blocks. These blocks are also nomenclatured as the metal-oxide (MO) arrester element. These are fundamentally ceramic materials, processed from a number of metal-oxide powders. The basic material used to manufacture metal-oxide varistors (MOV) are pulverized, very finely grained ZnO with average particle size of about 1 μm, to which as many as about 10 or more cations are added in the form of fine oxide powders. Its actual composition or recipe differs from manufacturer to manufacturer. The proportion by weight of all the additives together is about 10%, with the share of the individual components ranging from ppm to percent level. The purity and fineness of the metal-oxide powders and the homogeneity of the mixture are, therefore, of immense importance for the quality of the end-product.

To achieve the required homogeneity in the block the powder is treated in several processing steps. After mixing the powders slurry is prepared for spray-drying to obtain the dry granulates necessary for pressing. The resulting spheroidal granulates are about 50 μm in mean diameter with a wide distribution. Majority of the varistor devices are processed from this kind of powder except some category such as multilayer varistors which are made from a slurry paste. The manufacturing process to fabricate the arrester blocks is outlined in the flowchart of Fig. 3. In the sequence spray-drying operation is done twice, once before the calcining and the other after the calcining.

The spray dried powder in the form of granulates is compressed into disc-shaped blocks with approximately 55%–65% of their theoretical density. Pressing is performed by a uniaxial double action compaction technique. There are other ways to produce the blocks by the bi-directional pressing machine. Sintering of the disks is performed by a conventional sintering profile with a peak temperature of ranging between 1100°C and 1400°C having a total sintering cycle time ranging between 36 h and 48 h. The peak-sintering temperature often dictates the cycle-time. Therefore, sometimes the cycle-time may exceed 48 h. The sintered body takes the shape of a rigid cylinder possessing theoretical density exceeding 95% with shrinkage ranging between 15% and 20%. ZnO varistors undergo a liquid-phase sintering process. During this process, the bismuth oxide melts to form the liquid-phase which dissolves, at least in part, the other cations and presumably promotes their uniform distribution. The liquid-phase also favors the grain growth and dense sintering. Spinel precipitates, on the other hand, inhibit grain growth and help generate a uniform distribution of the ZnO grain size.

Sintering Configuration and Arrester Shape

The contact zone of a disc refers to the opposite faces which is remaining in the vicinity of the liner material during sintering process is more susceptible to failure. Upon deeper grinding of these two opposite faces can cause most of the failures. But sintering a disc without

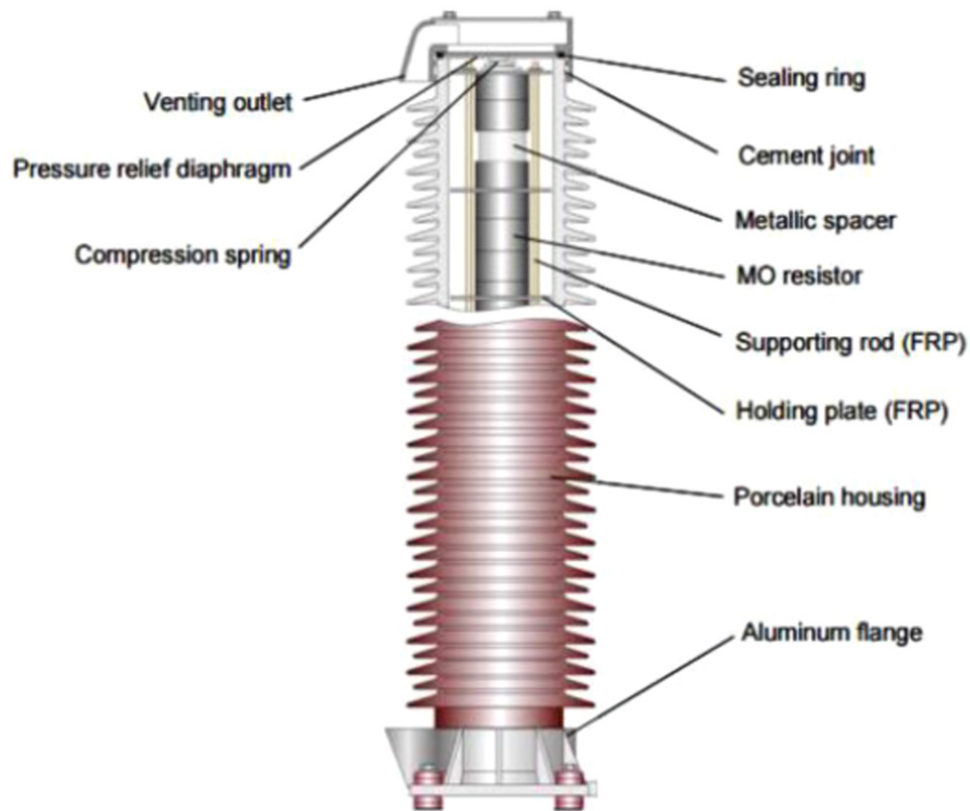


Fig. 2 Cross sectional drawing of porcelain housed metal-oxide arrester. Reproduced from Amotech Co., 2003. Introduction to chip Varistor. Available at: <http://www.docstoc.com/docs/162752017/introduction-of-chip-varistor—hweme>.

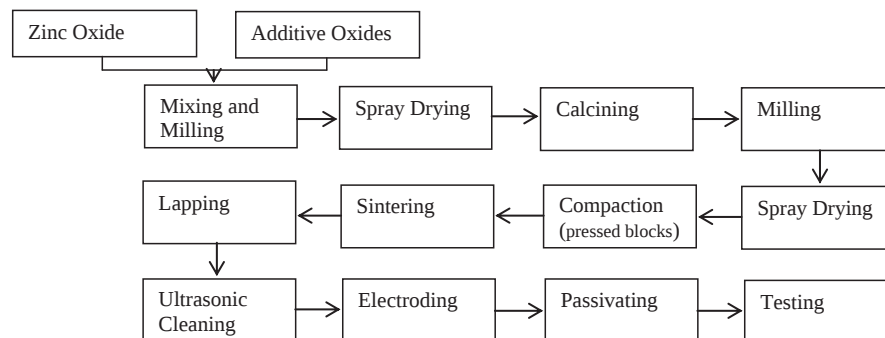


Fig. 3 Flowchart of the fabrication procedure of the ZnO arrester block.

keeping in contact with some sort of support is practically impossible. However, to minimize this undesirable effect, a number of alternative configurations have been attempted by changing the sintering orientation i.e., placing the disc on different kinds of support. Compared to the control (processed under standard condition), some of the arrangements demonstrated promising results.

The electrodes on the arrester block can be of two types – one, covering the entire flat surface, and two, keeping a little margin on the edge of the periphery. This little margin area implies non-electroded area. Both methods are industrially practiced to meet the specifications of the customers. The margin on the electrode appears to be helpful in preventing current from flowing through the vulnerable peripheral zone and, thus, reduce the number of failures in a lot. But in this method, there is undesirable effect too. A margin on the electrode obviously reduces the current carrying area of a disc and consequently lowers the effective volume for absorbing the energy injected by a pulse. This method, therefore, have an adverse effect on the energy absorption capability of a disc. So it is not apparent to conclude that the total effect from the two opposing factors. An experiment was undertaken to investigate the influence of the margin incorporated in the electrode by making these categories of disks.

The geometry of the disc also plays an important role on the performance. The failure mechanism is generally influenced by number of factors. Apart from the basic material properties the heat transfer mechanism can be a critical factor for steady state

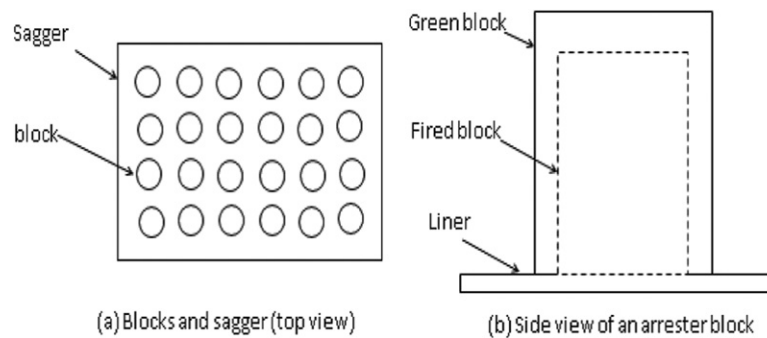


Fig. 4 Control orientation of arrester blocks on sagger for sintering (CSS).

operation. In this respect the geometry of the disc is very important. Commercial arrester blocks are available in cylindrical shape. An alternative design approach was attempted by providing a hexagonal shape to the arrester blocks.

The fracture mechanism of an arrester disc in short pulses with high amplitude of current is different from what is observed with long pulses in the energy test. Rupture or cracking is the main mode of failure. A theoretical study was conducted to correlate this fracture mechanism in the light of the theory on the propagation of stress wave. The fracture surfaces and the result of experiment conducted by two kinds of supporting metal block having different characteristic impedance were also found to be supportive of the theoretical predictions. Moreover, the speed of the longitudinal stress wave calculated on the basis of ZnO ceramic material was found to match closely with the measured celerity by LASER assisted technique.

Alternative Sintering Configuration

This investigation includes (i) the scope of alternative sintering configuration, (ii) the influence of margin on the electrode as the evaluation based on the data results on the (1) influence on the frequency of grinding, (2) energy absorption capability, and (3) high current performance. The objective of the study is to evaluate the feasibility of alternative liner support and sintering orientation of the arrester blocks. The sintered disks were characterized to evaluate the effect of the new method. In addition, to enhance the process capability in terms of the performance of the foreseeable advantages are (1) reducing the problem arising from regrinding, (2) minimizing the level of bismuth contamination from the liner material due to contact, (3) increasing the scope of repetitive use of the liner material, (4) lowering the allowance of block height for grinding, and (5) better geometry of the disc. The orientation of a varistor disc in the conventional sintering operation is given in Fig. 4.

The modified arrangement for this experiment is presented in Figs. 5 and 6. It should be mentioned here that for horizontal sintering, the V-groove supports were made from the fired arrester disks. To prevent sticking of the disks during sintering operation the supports were covered by spreading spinel powder. But the dried powder poured on the surface did not stick to it due to the inclination of the surface. To ensure proper adhesion of the dry liner powder with the inclined surface, it was necessary to lightly wet the supports by spraying water.

The spinel is known to have an inhibiting effect on the grain growth and its selection was attributed to keep the dimensional elongation along the contact to a minimum. These three orientations were selected for different purposes. The V-groove support can facilitate to keep the edges free from any physical contact during the sintering process. Thus improved faces with uniform edges were possible to achieve.

The fired smaller support system (Fig. 6 (a)) was chosen to keep the edges free from liner material to ensure good edge quality. The green support of the same diameter made from the standard varistor material (Fig. 6 (b)) was expected to yield the bottom edge unaffected from the adverse effects of sliding with sintered liner material during the shrinkage process. Like the conventional sintering process the green disks in these two arrangements were kept separated from the direct contact of the supporting liner by sparsely spreading the ZnO powder. The disks were categorized according to the cell description given in Table 1.

Importance of Grinding Operation

Grinding or lapping is needed in the fabrication of the ZnO varistor disks in order to:

- (1) Achieve required dimensional accuracy within tolerance limits,
- (2) Generate parallel opposite surfaces of the varistor disks with good edge quality,
- (3) Remove contaminated surface as skin effect, and,
- (4) Provide proper surface roughness for adequate adhesion of electrode material.

Regrinding a surface is needed when defects are observed by the physical inspection following the first grinding operation. Two types of defects such as the pinhole on the face and the chipping on the edges are usually detected. However, the size of the defect is important. Often a very small chip usually under some specified dimension is neglected. If the chip is big enough, the arrester disc may be rejected without further grinding depending whether it will satisfy the minimum target height. For any visible pinhole regrinding is recommended as its depth cannot be easily ascertained through physical inspection.

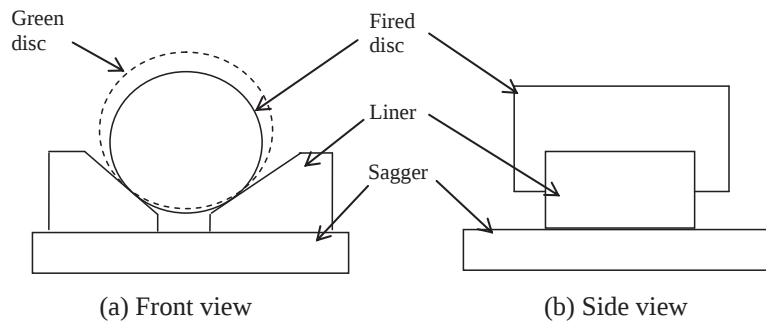


Fig. 5 Vee-groove support (VSS) for horizontal sintering orientation.

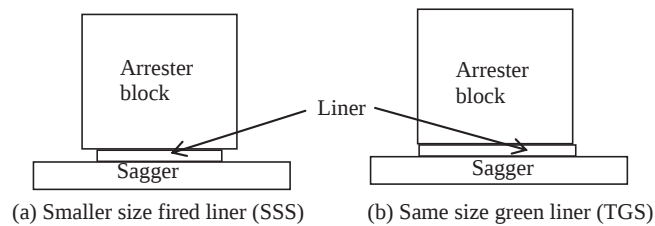


Fig. 6 Circular disc liner intended to improve the bottom edge (modified).

Table 1 Test condition and identification of various cells

Cell ID	Brief description of support system
CSS	Control support system (fired ZnO flat liner and extended ZnO powder)
VSS	Vee-groove support system (spinel powder in between contact)
SSS	Smaller sintered support system
TGS	Total green support system (allowing the bottom undisturbed shrinkage)

Regrinding is always an undesirable operation in the context associated with the cost, labor, equipment operation, and productivity. It is always preferable to have a process that can keep the figure regrinding to a minimum. In this experiment a considerable variation was observed among four cells indicating the significance of sintering configuration. **Fig. 7** shows the percentage of disks required for each cell to regrind. It is evident that the control is the worst in terms of the grinding operation. Disks sintered on the smaller liner (SSS) keeping the edge free of any contact are found to be the best. The VSS cell and TGS have exhibited considerably improved performance compared to the control block.

This grinding frequency is not uniformly distributed over the top and the bottom faces of the sintered arrester disks. A considerable difference was observed in the percentage share of regrinding among two surfaces. Since there is no scope of identifying the bottom or top for the disks sintered horizontally, the classification is not applicable for the VSS cell. The observation was, therefore, made for the rest of the three cells: CSS, SSS and TGS. The bottom surface was highly susceptible to defects which led to regrinding. The relative percentage of regrinding is shown in **Fig. 8**. It is noticeable that for the three cells there is no marked difference in the percentage share. The contact during sintering is certainly responsible to generate defects at the bottom surface. Any alternative process or liner material which can reduce the level of this contamination will be helpful in enhancing the varistor properties especially in terms of energy absorption capability and high current performance.

Alternate Shape of Varistor Disks

Research in the varistor technology have been primarily aimed at improving the fundamental properties. In this regard much of the work is related to the investigation of material composition, microstructure, whilst grain and grain boundary phenomena (Hinrichsen; Gambino *et al.*, 1987; Gupta and Miller, 1988; Yano *et al.*, 1992; Lee and Wiederhorn, 2004; Huang *et al.*, 2020; Balzer *et al.*, 2004) got maximum attention. Work investigating the effect of surface to volume ratio on the ZnO varistor properties especially in the context of energy absorption capability has not been reported. Energy absorption capability is an important functional characteristic of the arrester block. An enhanced functional life of a ZnO block can be assured through the improvement of this parameter leading to a more reliable electrical system. The shape of hexagonal cross-section was achieved by modifying the

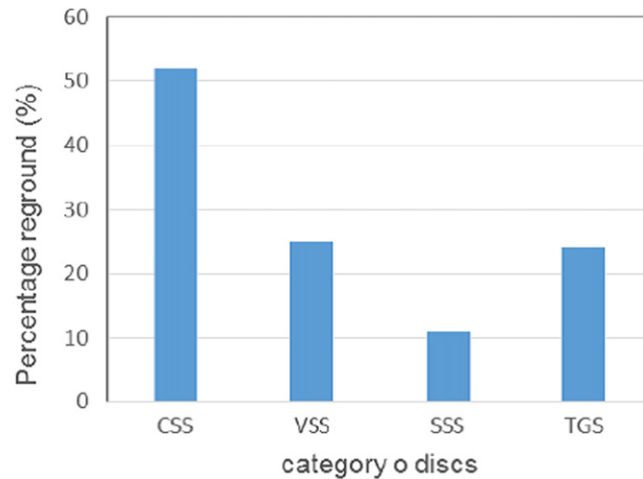


Fig. 7 Percentage of regrinding necessary for different cells.

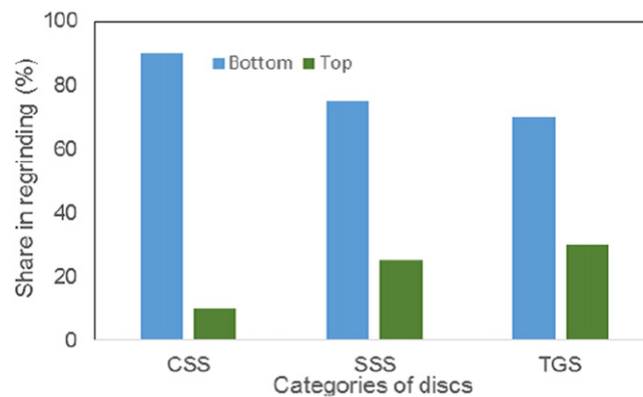


Fig. 8 Percentage share of the surface regrind on the top and bottom.

C-surface of the cylindrical disks as shown in [Fig. 9](#) in order to observe the effect of the surface to volume ratio of the arrester block on the energy absorption capability ([Karim and Begum, 2013](#)).

A cylindrical disc having diameter of 41 mm had cross-section area of about 13.2025 cm², and the cross-section area for a hexagonal disc was reduced to 10.9184 cm². Since the disc height of 42 mm remained unchanged, the volumes of the cylindrical and hexagonal disks became 55.45 cm³ and 45.86 cm³, respectively with the corresponding values of surface areas of 80.5032 cm² and 73.7887 cm², respectively. As a result, the S/V ratio of hexagonal disc is increased to a value 1.609 cm⁻¹ compared to the value for the cylindrical disc of 1.452 cm⁻¹. Thus, by making the modification of the cylindrical disc into hexagonal shape an increase of about 11% in the S/V ratio was achieved for the hexagonal disks.

Effect of Margin on Electrode

The margin on electrode looks to be advantageous in one respect but may be harmful in another sense. The effect was evaluated by considering the energy absorption capability. In [Fig. 10](#) the top and side view of the margin is given. The options were taken during electroding as: (1) control having a margin on electrode on both the surfaces, (2) One surface electrode with margin and the other surface fully electroded i.e., no margin, and (3) both surfaces electroded with no margin. These three categories of arrester disks were identified by CONT, OFFE, and BFFE, respectively.

Passivation Thickness: Application of the Collar Material

In varistor fabrication the passivation thickness plays an important role. It is applied on the peripheral cylindrical surface of the disks with a collar material that acts as a barrier to heat transfer during energy testing. US patent 4,046,847 A, US patent 3,959,543 A

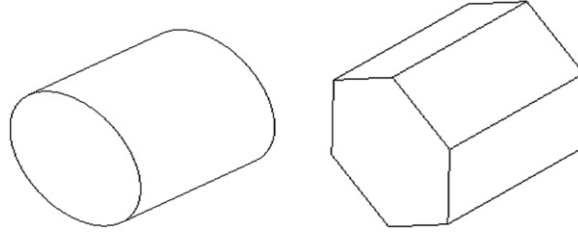


Fig. 9 Disc of hexagonal shape as obtained by grinding the cylindrical arrester block.

and US patent 5,096,620 A described different types of materials and its composition that can be used as passivating materials (Kresge, 1977; Ellis, 1976; Ditz and Paschke, 1992; Lytollis, 1994), whereas, US patent 5,307,040 portrayed ceramic materials as passivating materials for MOV and observed degradation or deterioration or failure behavior of the MOV block when subjected to an elevated temperature (120–130°C) at an AC/DC bias with 10% above the maximum continuous operating voltage (MCOV) for at least 250–1000 h (Karim *et al.*, 1997). However, there was no study of the influence of glassy collar material as the passivation thickness on the varistor performance, especially in terms of energy absorption capability. The passivation thickness was varied at three levels and failure mode was also observed.

Energy Absorption Capability and High Amplitude Short Duration (HASD) Test

Energy absorption capability is measured by millisecond rectangular pulses whereas high current performance is analyzed by HASD pulses of microseconds' duration. In both the cases highly accurate and reliable impulse test systems (Trigatron type 94 for energy and Impulse current test system WO 4924 for high current) were used. This characteristic of a varistor is determined by the maximum energy density injected into the ceramic body up to which it can sustain without failure for a cycle of three shots, expressed in terms of Joule cm^{-3} . Definition of the rectangular impulse current shown in Fig. 11(a) is a 2-millisecond pulse, conventionally termed as long wave. This kind of pulse is usually experienced in switching surges.

Energy injected by such a pulse is the integrated value of the product of the voltage and current passing through the disc over the pulse duration. So the amount of energy can be expressed mathematically with the following relationship:

$$\text{Energy} = \int_0^t v i \, dt \quad (1)$$

However, the instantaneous values of the voltage, v and current, i are not practically recorded. To evaluate the integrated energy the peak values of the clamping voltage and peak current passing through the arrester block are used. For a pulse of quasi-rectangular shape as demonstrated in Fig. 11(a), the relationship can be expressed in terms of the peak voltage, V_{pk} (kV) and peak current, I_{pk} (A) for a duration of time T in millisecond as follows:

$$\text{Energy} = \int_0^t v i \, dt = KV_{pk}I_{pk}T \quad (2)$$

where K is a constant, dependent on the wave-shape. For a pulse as shown in Fig. 11(a), the value of K is taken as 1.14. Thus, the total injected energy by is estimated as $2.28V_{pk}I_{pk}$. The HASD pulses are in the range of microseconds' duration. This is a simulated pulse of the actual lightning stroke. Typical short pulse used for evaluating high current performance is $4 \times 10 \, \mu\text{s}$ (Fig. 11(b)) where the first value (virtual front time) indicates the rise time from 10% to 90% of the peak current and the second value (virtual time to half value) is the duration to reach to 50% of the peak during fall.

Unlike the measurement of mechanical strength, the test for the energy absorption cannot be performed in a single step. Testing is initiated with a lower charging voltage so that the injected energy remains in the lower range, say, about 200 Joule cm^{-3} , to minimize the likelihood of failure at the first cycle. The testing by discrete increment of charging voltage and cooling of the disks is a tedious process which is continued until all the disks fail at a certain stage.

Since this is a destructive test, a sample of few disks is taken from a lot. Unlike the test for the energy absorption capability, only one shot is applied at a time for the high current capability. The failure mode in this case is predominated by cracking rather than by the thermal runaway or puncture as observed in long pulse test. A parameter to express the high current performance of a particular cell can be defined mathematically (Karim *et al.*, 1997; Evans, 1991) in the following form:

$$\text{High Current Performance (\%)} = \frac{\sum n_i x_i}{\sum N X_i} (100) \quad (3)$$

where N = initial sample size of the disks to be tested, X_i = rated peak current at the i th pulse, n_i = number of disks successfully passing the i th pulse, and x_i = actual peak current in the i th pulse.

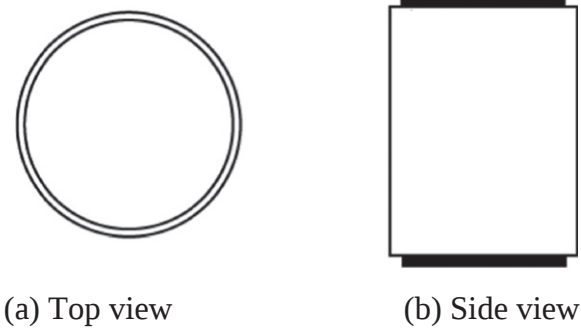


Fig. 10 Electrode with margin as shown on the face of an arrester block.

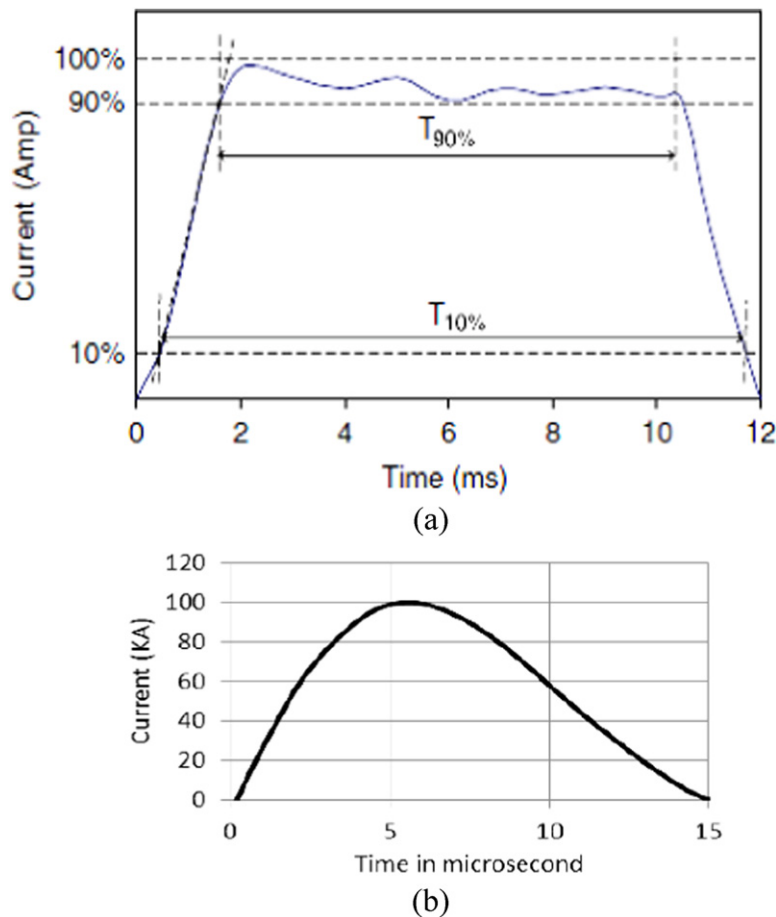


Fig. 11 (a) Long (ms) pulse for energy absorption and (b) HASD ($4 \times 10 \mu s$) pulse for high current performance.

Energy Testing for Disks With Different Sintering Orientation

The test for energy also known as the “strength test to destruction” whereby, 10, 12, 14, and 16 samples were taken for CSS, VSS, SSS and TGS cells, respectively. The results are depicted with the error bar in Fig. 12(a). In terms of the energy absorption capability there is no significant difference among the first three cells with slightly higher value for SSS category. But, the mean energy absorption capability for the disks sintered on the same size green support (cell TGS) is about 10% less compared to the other cells.

It may be mentioned here that both the surfaces of a disc are cleaned by grinding operation. As recorded and shown in Fig. 12(b), the category (SSS) looks promising followed by (VSS) and (TGS) in the context of the need of minimum regrinding frequency of the surfaces. According to the level of energy absorption capability and regrinding frequency the disks belonging to the SSS cell are superior. But due to the smaller size of the support, placement of the disks on top of it and subsequent handling of the saggars to position inside the furnace for sintering purpose are difficult. Thus, this unstable support system cannot be recommended.

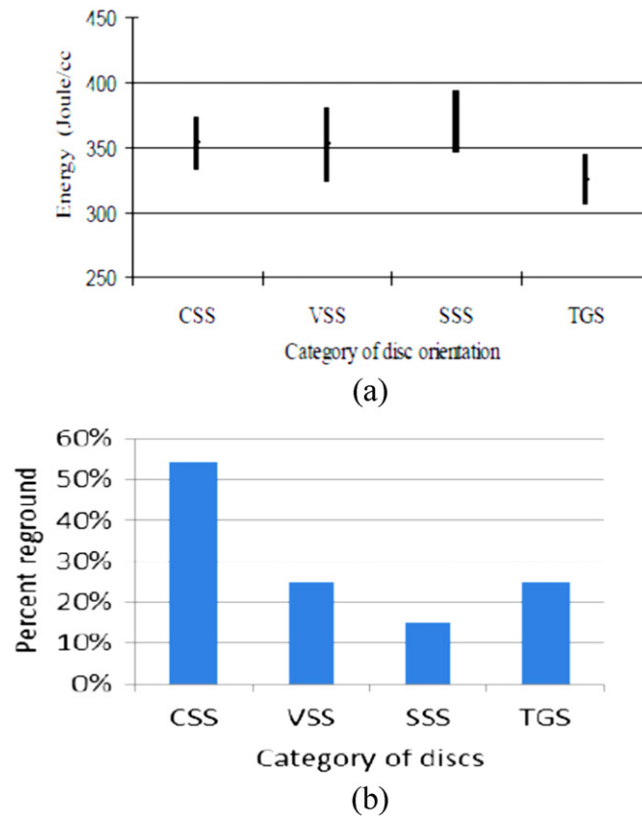


Fig. 12 (a) Mean energy absorption capability of different cells (b) Percentage of disks needing regrinding as change of sintering orientation.

For high current performance multiple disks from each of the cells for sintering orientation were tested. The rated current was selected with an increment of 5 kA for every subsequent shot for every disc. The starting current was 100 kA and there were no survivors after 115 kA shot. Based on the values of high current performance parameter as defined by Eq. (3) the relative performance is presented in Fig. 13. So according to the combined performance on three characteristics such as energy absorption capability, frequency of regrinding, and high current performance, the choice of horizontal sintering on Vee-groove support (VSS) appears to be reasonable.

Energy Test for Different Shape of Arrester Blocks

To compare the energy absorption capability a total of 20 arrester blocks (10 cylindrical and 10 hexagonal) was taken. Fig. 14 depicts the cumulative percent failure with respect to increasing level of energy. Failure of arrester blocks in the test for energy absorption capability is usually dominated by occurrences of pinhole and flashover. For very few cases disks failed with crack or fracture alone. The failure mode and the location of damaged marks for each of the disks have been tracked and it has been observed that pinhole accompanied by a flashover is a very common mode of failure. Since the hexagonal disks were prepared by grinding the side surface of the cylindrical disks, variation in energy absorption capability could possibly be linked with the removal of the presumably contaminated surface of the cylindrical disks. But no such link can be validated or ascertained from the observations of the failure patterns and their distribution.

Effect of Margin of Electrode on Energy Absorption Capability

The performance of arrester blocks with variation of electrode margins is presented in Fig. 15. The sample size was 17, 16, and 15, respectively for CONT, OFFE and BFFE, respectively. The injected charging was initiated with voltage of 24 kV which had equivalent energy of $140 \text{ Joule.cm}^{-3}$. The testing was continued up to 49.9 kV with subsequent increment of 1.2 kV for each test cycle. But it was unusual that even at that stage out of 48 disks only 18 failed while the rest 30 disks survived. Energy absorption capability of the survivor disks was computed on the basis of data obtained at the last cycle of test at the charging voltage of 49.9 kV at the generator. In the legend the letters "F" and "S" in parenthesis stand respectively for the failed and survived disc. Among the survivor disks, it is evident that the disks of BFFE and OFFE cells absorbed more energy than those of the CONT.

The observed effect is attributed to the full-face electrode leading to more current carrying cross-sectional area. However, in this regard no difference observed between the BFFE and OFFE. Since it is not clear from the illustration in Fig. 15 about the influence

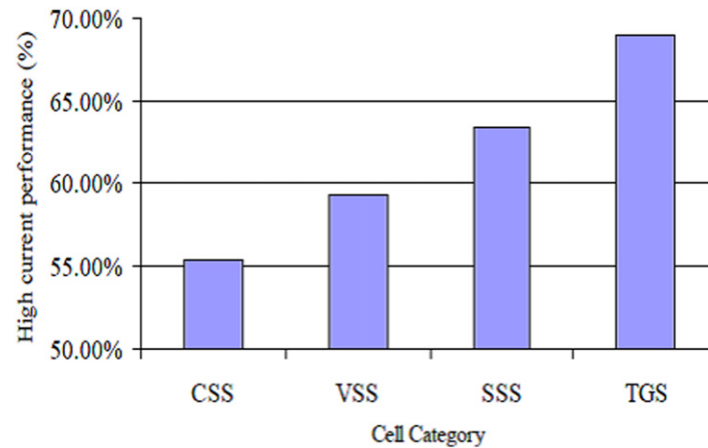


Fig. 13 High current performance as affected by sintering orientation.

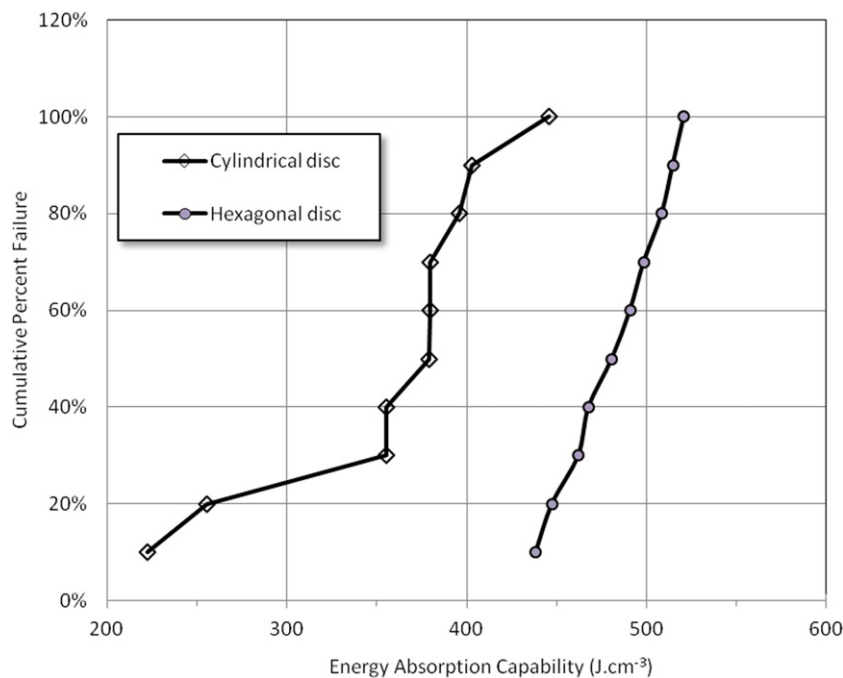


Fig. 14 Variation of energy absorption capability due to change in geometry of the arrester block from cylindrical to hexagonal shape.

of electrode on the energy absorption capability, the percentage of disks survived after the maximum possible energy injection for the three cells is presented in Fig. 16. It is apparent from the consistent trend of higher survival rate that the full face electrode is conducive to energy absorption capability. Some unsatisfactory results with full face electrode is not unlikely when the quality of passivation and its thickness are not properly maintained. Moreover, bismuth contamination can also facilitates the failure, as the additive Bi_2O_3 is transformed to liquid at high temperature and a portion of it can accumulate on liner at bottom face if the liner is not flat. It is obvious from Fig. 17 the survivor from bismuth contamination is much lower.

The level of contamination is directly related to failure. When arrester disks were categorized depending on the affected area as slightly, moderately and highly contaminated. After test the failure rate was found to be different for the three subgroups as shown in Fig. 17. Horizontal sintering will be very helpful in this regard. The liquid bismuth will not be able to accumulate on the inclined supporting surface. As a result there will be no scope of contamination from the liquid bismuth.

Passivation Thickness: Energy Absorption Capability

The cumulative plot of the energy absorption capability of the varistors with different glass thickness is presented in Fig. 18, and the mean energy with standard error is illustrated in Fig. 19. The standard amount of glass taken as the minimum level in the experiment had shown inferior performance and the varistor started to fail at very low energy level. Nevertheless, the heaviest

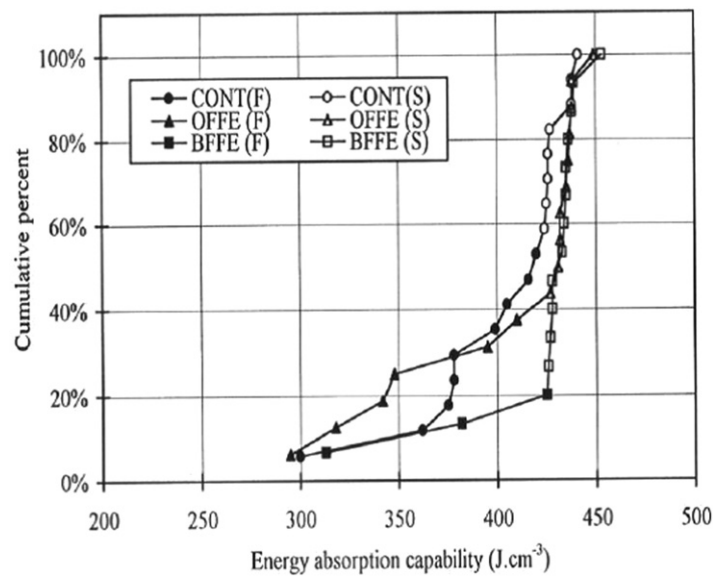


Fig. 15 Effect of electrode on energy absorption capability.

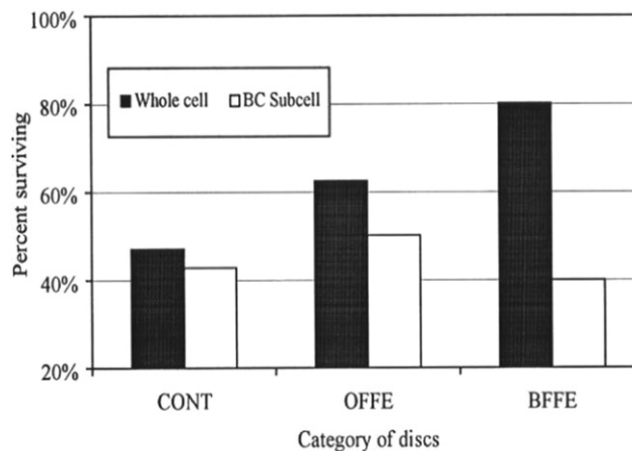


Fig. 16 Percent survived of individual cell and bismuth contaminated sub-cell.

coating did not exhibit the best energy absorption capability. It is also noticed from Fig. 18 that for the best cell, 50% of the disks survived after 400 J cm^{-3} .

Stress Wave in HASD Test and Failure Mode

The treatments made in the context of rigid dynamics and the theory of elasticity are sufficiently accurate for the problems in which the time between the application of a force and the setting up of effective equilibrium is short compared with the times in which the observation is made (Huang *et al.*, 2019). But when we consider the effects of forces which are applied for only short period of time, or are changing rapidly, the effects must be considered in propagation of stress waves.

The theory of propagation of stress waves in solids was developed during last century. But this was in many ways in advance of experimental work, as there were then no methods available for observing the passage of stress waves on a laboratory scale. But in recent times due to advent of electronic techniques to generate and detect elastic waves of high frequency, the field is getting a new boost.

The finite velocity of stress wave in a fluid of density, ρ and the bulk modulus, k can be inferred directly from the equation of motion as $\sqrt{(k/\rho)}$. This is the only type of wave motion which is propagated through a medium which cannot sustain finite shear stresses. However, in extended isotropic solids, two types of waves may be propagated. These are waves of dilation (longitudinal wave) and distortion (transverse wave). The wave of dilation travel with a velocity $\sqrt{[(k + 1.33 \mu)/\rho]}$, μ being modulus of rigidity,

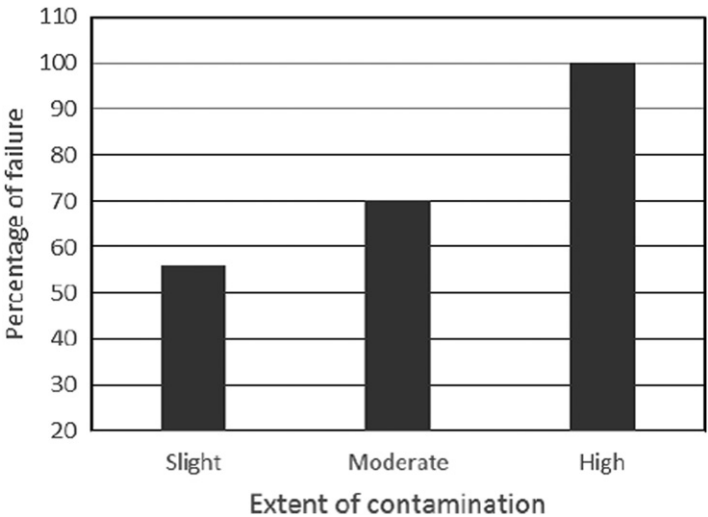


Fig. 17 Trend of failure with the level of bismuth contamination.

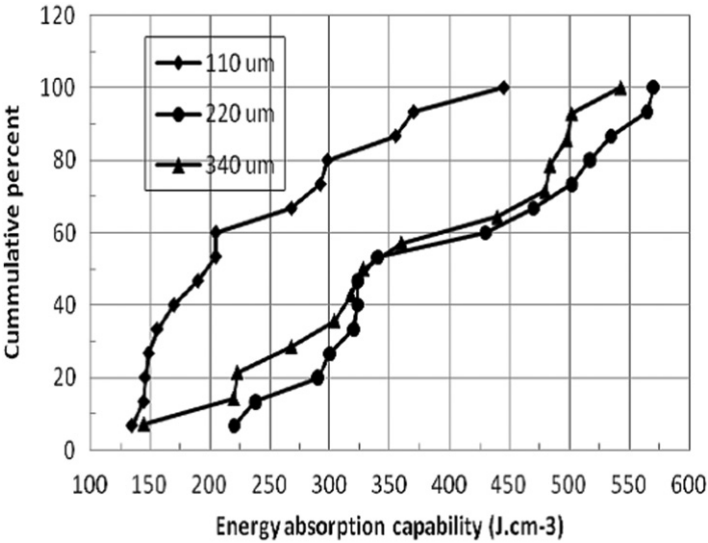


Fig. 18 Energy absorption capability of varistors having different glass thicknesses.

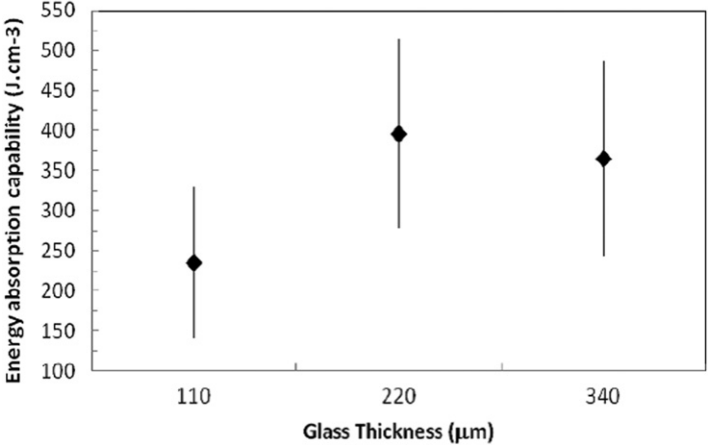


Fig. 19 Mean energy absorption capability with $\pm$ standard deviation of the varistors having different glass thicknesses.

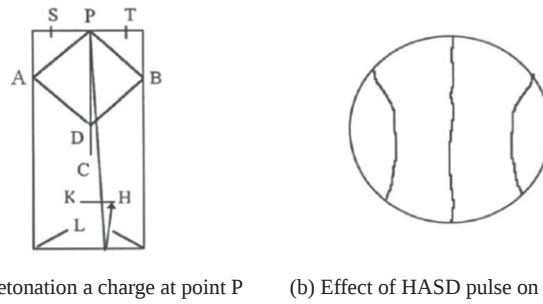


Fig. 20 Comparison of fracture locations produced in the two sources.

and the wave of distortion travels with a velocity $\sqrt{[\mu/\rho]}$. When a solid medium is deformed, both distortional and dilatational waves are normally generated and propagated.

Fracture Produced by Stress Waves

When a stress pulse of sufficiently large amplitude travels through a solid it may produce fractures. The fractures produced by stress pulses differ from those produced statically. This occurs firstly, because of the velocity of crack propagation is considerably lower than the velocity of propagation of pulse. Secondly, with a short pulse only a small part of the specimen is stressed at any one time and fractures may form in one region of a specimen quite independently of what may be occurring elsewhere. Thirdly, when a compression pulse is incident on a free boundary it gives rise to a reflected tension pulse, while when it is reflected obliquely both a dilatational (longitudinal) and distortional (transverse) pulses are produced.

Comparison of Fracture Originated by Stress Wave and High Current Pulse

When a charge is detonated at the center of one face of a cylindrical specimen a number of different fracture regions are formed (Huang *et al.*, 2019; Kolsky, 1963) as shown in Fig. 20(a). Similar fracture regions are observed for a cylindrical arrester block in high current test, shown in Fig. 20 (b). A circular crack on the top surface a few millimeters from the edge as shown in by S and T results from the reflection of the compression pulse at the cylindrical surface of the specimen as a wave of tension. A linear region of fracture extending for some distance PC, the axis of the cylinder, produced by the wave reflected from the curved surface converging on to the axis of the cylinder so that a very large tension is built. Similar fracture modes are frequently observed in case of high current test. Though it is subjective to individual mechanical properties of the disc material, a low volt arrester is not expected to sustain high current more than 9–10 kA/cm². For a high voltage arrester of the same height the current density must be lower to cause fracture as the amplitude of the energy in this case becomes higher for the same level of current.

The geometry of an arrester plays an important role in the failure mechanism. This occurs in arrester blocks having lower aspect ratio (H/D) are found to be accompanied by the longitudinal crack as presented by line PC. But in this case the circular crack at the edges as shown in Fig. 20(b) is very common. Arrester block with higher aspect ratio are found to be susceptible to transverse fracture (waist crack). A part's resonant frequencies are determined by its dimensions, the density and the elastic constant of the material. Increasing the length lowers the resonant frequency of the bending mode. The "waist failure" in case of arrester disks having a higher aspect ratio appears to originate from the failure due to the first injection of short pulse is very important. Because depending upon this parameter, the mode of vibration of the disc will change. If the excitation frequency matches with the resonant frequency much larger vibrations are generated and can cause earlier failure.

Fracture Surfaces in HASD Pulse and Diametral Compression Test

The fracture surface generated by the tension in the diametral compression test of an arrester specimen was found to be different than that was observed in case of high current performance test. In the latter case a number of ripples are observed on the fractured surface which resemble to the stress waves propagated through a Perspex specimen (Kolsky, 1963) as shown in Fig. 21.

An arrester draws current uniformly throughout the flat face and the center of the face will be the location of peak stress wave. But if there is any preferential path the location of resultant stress wave may be shifted. In that context, the fracture locations may be slightly deviated. The fracture surface of a typical failure in HASD test and that in diametral compression test are presented in Fig. 22.

Speed of Stress Wave in ZnO Varistor Material

The general relationship (Kolsky, 1963) for the speed of stress wave propagation, C consists of the Lamé's constant λ , μ and the density ρ , of the material. The equation of dilatational wave propagation is as follows:

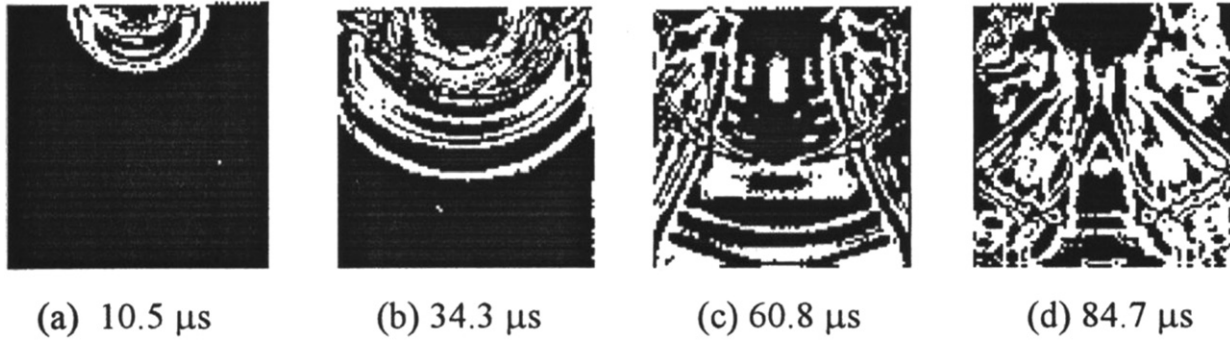


Fig. 21 Stress wave generated by detonating a charge of lead azide on the center of upper face of a Perspex parallelepiped specimen.

$$C = \left[\frac{(\lambda + 2\mu)}{\rho} \right]^{\frac{1}{2}} \quad (4)$$

This stress wave speed in the metal oxide varistor material can be estimated on the basis of elastic properties for ZnO ceramic. Since the bulk of the constituent materials of the varistor is zinc oxide, the result should not deviate too much from the actual value. The Young's modulus, E is derived as function of Lamé's constant λ and μ . The relationship of which is as follows:

$$E = \frac{\mu(3\lambda + 2\mu)}{(\vartheta + \mu)} \quad (5)$$

The shear modulus, μ is expressed in the terms of Young's modulus, E and the Poisson's ratio, ν as in equation:

$$\mu = \frac{E}{2(1 + \gamma)} \quad (6)$$

Thus the Poisson's ratio ν can be solved as follows:

$$\vartheta = \frac{\lambda}{2(\lambda + \mu)} \quad (7)$$

But for a particular material, the Young's modulus decreases with the level of porosity in the material. A relationship between the modulus of elasticity and the porosity volume fraction of the material (Richerson, 1982) is given by:

$$\frac{E}{E_0} = \exp(-\beta p) \quad (8)$$

where E_0 = Young's modulus of fully dense material, P = porosity volume fraction = $1 - (\rho/\rho_0)$, and β = constant ($2 < \beta < 4$).

Now for the pure and fully dense zinc oxide ceramic (McColm, 1990) the density $\rho_0 = 5.68 \text{ gm/cm}^3$, the Young's modulus, $E = 123.5 \text{ GPa}$ and the shear modulus, $\mu = 45.7 \text{ GPa}$. The Poisson's ratio, ν can be worked out from the equation as 0.35.

For any assumed density of varistor material, the elastic parameters can be evaluated for a specific value of β . Taking $\beta = 4$, the velocity of dilatational wave for the ZnO material was calculated by the Eq. (4) as a function of fired density. By adopting similar method the velocity of dilatational wave for ZnO material was calculated theoretically and plotted against density as shown in Fig. 23.

Analytical and Measured Speed of Stress Wave in ZnO Varistor

The non-contact and non-destructive testing method to be developed for detecting the defects or flaws in varistor material is based on the phenomena of imparting optoacoustic pulses and its propagation in the disc. The varistor blocks were equipped with CO₂ or YAG laser and a piezoelectric sensor. By the laser a single pulse was imparted on the flat surface of the arrester disks and the sensor in the opposite face receives the signal propagated through the disc body. With the elapsed time the speed of propagation of the acoustic wave (celerity) in the ceramic block is determined.

The literature suggests that the pulse propagation is dependent on the basic elastic properties and the density of the medium, not on its grain size. The elastic modulus is also dependent on the porosity-increasing porosity decreases elastic modulus. In Fig. 23 some of the available data [from an international report] are inserted. The practically found celerity is found to be in very good agreement with theoretical results.

The fundamental relationship of the propagation of the stress wave in solids in terms of the elastic constants and density is verified for the ZnO varistor material. Grain size of the material does not play any significant role. Experimental results also obtained in the measurement of celerity are also supportive of this characteristics feature.

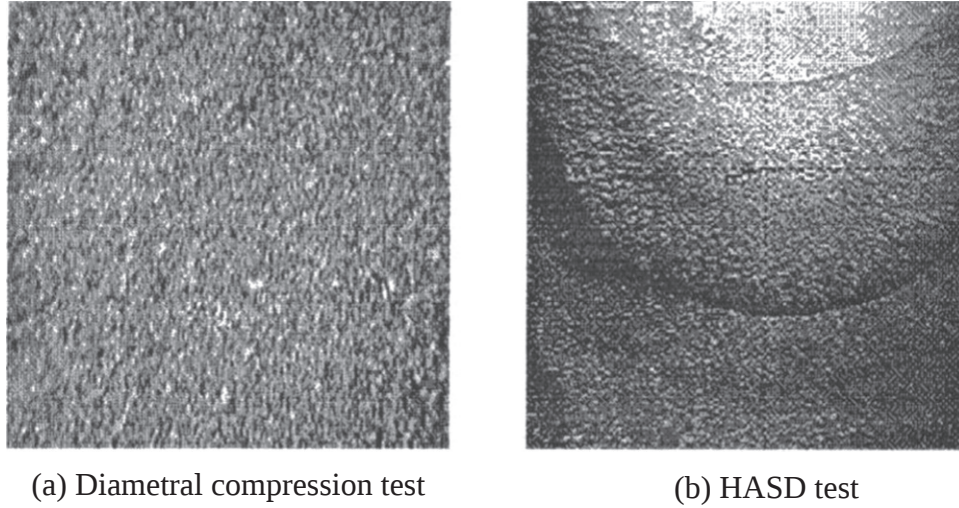


Fig. 22 Fracture surface developed under different test conditions.

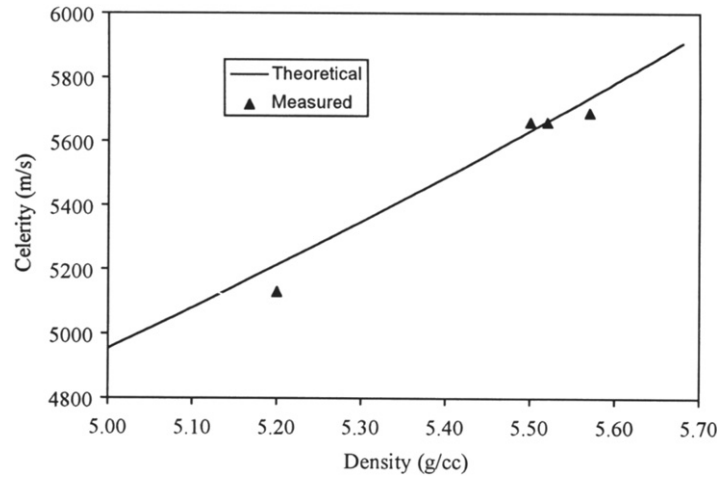


Fig. 23 Theoretical and measured celerity of ZnO varistor material.

Reflection of Stress Waves and Observed Influence in High Current Pulse

When an elastic wave reaches a slip free boundary four waves are generated. Two of them are reflected into the second medium and two are reflected back as shown in Fig. 24.

But the waves of distortion A_3 and A_5 vanish (Evans, 1991), so that only dilation waves are generated. The solution of the amplitude A_2 of the wave reflected back into the first medium is given by

$$A_2 = \frac{A_1(\rho_b c_3 - \rho_a c_1)}{(\rho_b c_3 + \rho_a c_1)} \quad (9)$$

So the amplitude of the reflected stress wave depends on the quantity $(\rho_b c_3 - \rho_a c_1)$ where ρ_a and ρ_b are the densities of the first and second medium and c_1 , c_3 are the corresponding velocities of dilatation. It is apparent that no wave will be reflected at the media. This product ρc is sometimes known as the characteristic impedance of the medium. An experiment was carried out on the basis of theory to evaluate the effect of supporting materials in the case of the test for high current. The results were found to be supportive to the prediction of above proposition.

In the HASD test, the supporting blocks as shown in Fig. 25 are usually made of aluminum, whose characteristic impedance, ρc is $1,706,400 \text{ gm cm}^{-1}\text{s}^{-1}$. But for mild steel the impedance is $4,633,200 \text{ gm.cm}^{-1}\text{s}^{-1}$. Now for the varistor material the characteristic impedance is $3,220,000 \text{ gm cm}^{-1}\text{s}^{-1}$. So in the context of the Eq. (9), when aluminum block is used, the amplitude of reflected wave will change its sign and there will be no change in phase on reflection. But when mild steel will be used the situation

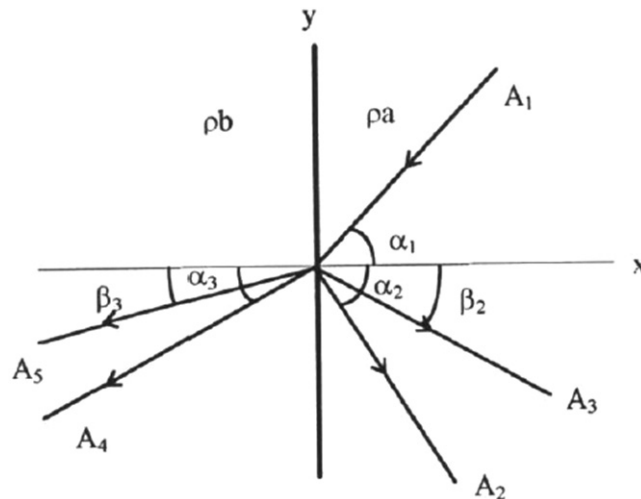


Fig. 24 Reflection and refraction of incident dilatation wave at plane surface.

will be opposite as its characteristics impedance is higher than the varistor material. So a test on mild steel support is expected to generate more reinforced stress wave resulting in more failures.

The phenomena was tested randomly categorizing the blocks into two groups—one of which was tested using aluminum block while the other using the mild steel block as support as shown in Fig. 26. They were subjected to HASD test with increasing rated current until all the disks failed. The rated currents were 94, 99, 103, 105, 106, and 107 kA. The plot in Fig. 25 shows the cumulative percent failure as function of actual recorded current at which the disks failed.

The fracture of arrester blocks initiated in the high current test may be prevented by adopting measures in the context of stress wave. Some kind of suitable reinforcement can be included in the formation of the ZnO varistor which will enhance its mechanical strength. The selection of the passivation material should take into account the reflection criterion.

Materials having lower reflective index than the presently used glass could be helpful in reducing the amplitude of the reinforced waves reflected from the side of the surface of the disc. Probably this is one of the reasons for having an improved high current performance form the other kind of passivation material. In terms of characteristics impedance, choice of aluminum as the supporting block at the end of an arrester assembly stack appears to be appropriate.

Vibration and other effects of stress wave developed during high current impulse are necessary to be considered to select the geometry of an arrester block. Selection of an arrester geometry should take into account in resonant frequency. Smaller height will maximize the resonant frequency of the disc and can help keep the failure rate in high current test to a minimum. This is especially observed in case of test on a stack of smaller disks—as practically no failure is found to occur through ‘waist failure’.

It is found that superior performance is achievable in HASD test when arrester blocks are kept under higher pressure by applying load through the contact support. The better gripping or contact between the faces of the support and the arrester block is expected to be helpful in this regard. But there is disadvantage of this arrangement. Arrester block kept under high pressure will increase the leakage current (Gupta, 1990) and eventually its life will be reduced.

Failure Analysis: Alternate Shape of Arrester

To compare the energy absorption capability a total of 20 arrester blocks (10 cylindrical and 10 hexagonal) was taken. Tests were continued until all of them failed. The peak values of the clamping voltage on each arrester block and the peak current passing through it were recorded. The values of the clamping voltage (kV) and peak current (Amp) as sustained by the disks are presented in Tables 2 and 3. These values represent the clamping voltage and current of the last cycle of three shots sustained by the individual disc.

As mentioned earlier the energy absorption capability of a disc is calculated by using Eq. (3) taking into account the clamping voltage and the peak current from the last cycle of three shots sustained by the disc. Since the three shots slightly differ in terms of the clamping voltage and current, an average energy injection has been used in estimating the energy absorption capability for both the cylindrical and hexagonal disks. Fig. 24 depicts the cumulative percent failure with respect to increasing level of energy.

Failure of arrester blocks in the test for energy absorption capability is usually dominated by occurrences of pinhole and flashover. In a very few cases disks failed with crack or fracture alone. The failure mode and the location of damaged marks for each of the disks has been tracked and recorded as presented in Table 4. Pinhole accompanied by a flashover is a very common mode of failure. Since the hexagonal disks were prepared by grinding the side surface of the cylindrical disks, variation in energy absorption capability could possibly be linked with the removal of the presumably contaminated surface of the cylindrical disks. But no such link can be validated from the observations of the failure patterns and their distribution. Out of ten disks for each set of control and hexagonal disks there is no significant difference both in failure mode and the location of the mark or origin of failure. In both

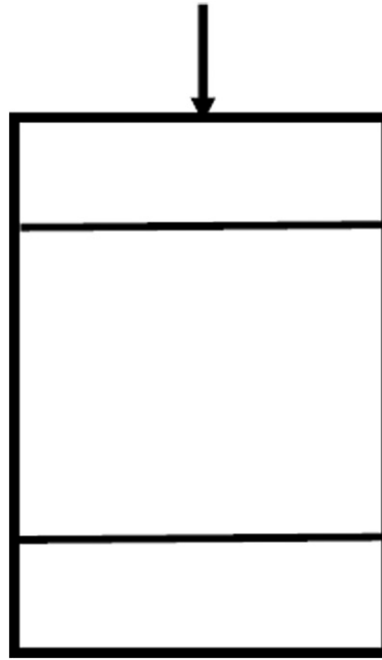


Fig. 25 Arrangement of arrester block in the HASD test.

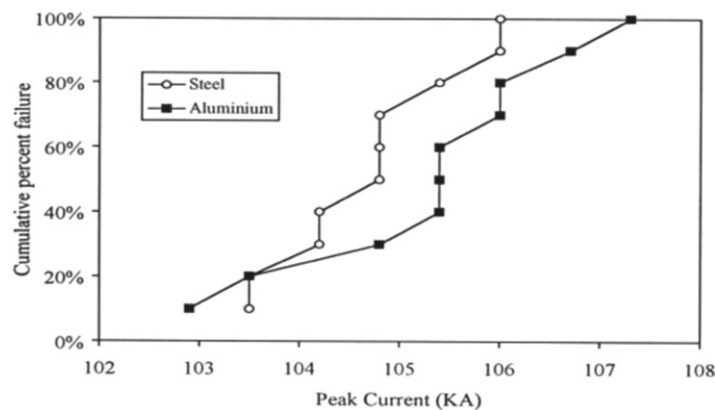


Fig. 26 Effect of supporting materials on the high current performance.

the cases, only one disc from each set exhibited failure solely through flash over, 5 and 4 failures by pinholes occur respectively for hexagonal and cylindrical disks.

An arrester block is cylindrical in shape with two flat surfaces. Injected energy from the stroke of transient electrical surge into the arrester body is transformed into heat and dissipated through the surface of the disc body. Hexagonal disks having higher surface to volume (S/V) ratio exhibited enhanced energy absorption capability. The round side or C-surface of the cylindrical disc was transformed into hexagonal shape by grinding. For this case the S/V ratio of hexagonal disc is increased to 1.609 cm^{-1} compared to the value 1.452 cm^{-1} for the cylindrical disc. Thus by making the modification of the geometrical shape about 11% increase in S/V ratio was achieved for the hexagonal disks. Following the other processing steps, ZnO arrester blocks of both shapes were made and tested for energy. Like mechanical strength measurement, the sample of disks do not fail at a particular value of the energy absorption capability, rather it follows a distribution. Average energy absorption capability can be an indicator for the relative performance. The disks having hexagonal shape have an average of 483 J cm^{-3} energy absorption capability while the disks having the cylindrical shape yielded an average of only 357 J cm^{-3} . Thus, about 35% increase in energy absorption capability is observed for the hexagonal disks. In this test the electrical pulses applied is of 2 only millisecond duration and the arrester is considered to be heated adiabatically. But the sample of hexagonal disks having higher surface to volume ratio has exhibited improved energy absorption capability. This phenomenon can be attributable to the effect of increased surface to volume ratio of arrester block. The knowledge of the influence of S/V ratio can be applied in designing the geometry of the device for improved functional reliability of electrical system.

Table 2 Clamping voltage and peak current sustained by the cylindrical disks

SL #	First shot		Second shot		Third shot	
	Volt (kV)	Current (A)	Volt (kV)	Current (A)	Volt (kV)	Current (A)
C1	10.97	486	11.37	477	11.65	470
C2	11.56	528	12.02	519	12.30	511
C3	11.88	715	12.45	702	12.52	692
C4	11.90	714	12.47	702	12.53	692
C5	11.77	772	12.33	758	12.31	750
C6	11.83	769	12.36	755	12.36	748
C7	11.22	810	11.73	796	11.65	794
C8	11.36	836	11.89	821	11.82	814
C9	11.20	865	11.72	848	11.52	846
C10	12.48	858	13.04	843	12.91	837

Table 3 Clamping voltage and peak current as sustained by the hexagonal disks

SL #	First shot		Second shot		Third shot	
	Volt (kV)	Current (A)	Volt (kV)	Current (A)	Volt (kV)	Current (A)
H1	12.40	707	12.96	687	12.82	684
H2	12.90	695	13.44	676	13.26	674
H3	12.76	725	13.27	707	13.03	709
H4	12.73	725	13.25	707	13.65	705
H5	12.88	749	13.30	730	13.25	728
H6	12.63	769	13.14	762	12.94	764
H7	12.18	819	12.63	800	12.40	806
H8	12.62	808	13.05	790	12.81	794
H9	12.22	844	12.64	825	12.40	831
H10	12.42	842	12.82	821	12.56	831

Table 4 Failure mode, location and effect observed upon completion of the energy test

Disc ID	Energy (J/cm ³)	Failure mode and effect			Location of failure mark	
H1	438	Pinhole	–	Small crack	Top	Center
H2	447	Pinhole	–	–	Bottom	Corner
H3	462	Pinhole	–	Fracture	Bottom	Center
H4	468	Pinhole	Flashover	–	Top	Corner
H5	481	Pinhole	Flashover	Small crack	Top	Center
H6	491	Pinhole	Flashover	–	Bottom	Periphery
H7	498	Pinhole	–	Fracture	Bottom	Center
H8	508	Pinhole	Flashover	Fracture	Top	Center
H9	515	–	Flashover	–	Bottom	Periphery
H10	521	Pinhole	–	Fracture	Bottom	Center
C1	222	Pinhole	Flashover	–	Bottom	Periphery
C2	255	Pinhole	–	–	Bottom	Periphery
C3	355	–	–	Small crack	Bottom	Center
C4	355	Pinhole	Flashover	Fracture	Top	Periphery
C5	379	Pinhole	Flashover	–	Bottom	Periphery
C6	379	Pinhole	Flashover	–	Bottom	Periphery
C7	379	Pinhole	Flashover	–	Bottom	Center
C8	396	Pinhole	–	–	Bottom	Center
C9	403	–	Flashover	–	Bottom	Periphery
C10	446	Pinhole	–	–	Bottom	Center

Table 5 Failure mode of varistors with different glass coatings during “strength to destruction” test

Glass thickness (μm)	Sample size	Failure mode						
		Interface	Pinhole (ph)	Flashover (fo)	Rupture	Interface + fo	Interface + ph	ph + fo
110	15	8	3	–	–	3	–	1
220	15	3	4	–	4	3	–	1
340	14	–	8	–	2	2	–	2

**Fig. 27** Failure mode of the varistors during destruction testing having different glass thicknesses.**Table 6** Analysis of variance for the energy absorption capability of varistor with various glass thicknesses

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F_{cal}	F_{tab}
Treatment	225,721	2	112,861	9.858	3.234
Error	469,384	41	11,448		
Total	695,105	43			

Variation in Passivation Thickness

The coating of the glass acts as an insulator and resists the heat transfer. The effect is more obvious in the second and third shot in the energy test. The heavier coating acts as higher insulator and does not dissipate heat as effectively as the lower thickness. Thus, the high temperature in the ceramics makes it more vulnerable to failure. This feature is supported by the fact that the thicker coating failed through the ceramic and most of the disks failed by electrical puncture as presented in [Table 5](#). The mode of failure was also categorized and illustrated in [Fig. 27](#). It is clear from the Figure that the increase of glass thickness has shifted the failure. More than 85% of the varistors failed through the ceramic coated with thicker passivation coating compared to 27% in the case of the thin coating.

The variance analysis of the varistors with different glass thickness is given in [Table 6](#). At 95% confidence interval the tabulated F-statistics at $\gamma_{2,41}$ is less than F_{cal} . Hence the glass thickness has significant influence on the energy absorption capability of the varistor.

Conclusions

Reliability of a surge protection system is largely dependent on the energy absorption capability. Injected energy from the strokes of transient electrical surge into the arrester body is transformed into heat and dissipated through the surface of the disc body. Higher S/V of the hexagonal disc is found to be highly conducive in heat transfer leading to enhanced life. A hexagonal disc having S/V ratio of 1.609 cm^{-1} compared to 1.452 cm^{-1} for the cylindrical disc has led to an increase of about 11% in S/V ratio. But the average energy absorption capability for the hexagonal disks was found to be 483 J cm^{-3} compared to that of 357 J cm^{-3} for the disks having the cylindrical shape. This is equivalent to an increase of about 35% in energy absorption capability. Thus the effect of increased surface to volume ratio of arrester block cannot be ignored. Moreover, disks with the hexagonal shape can be produced

as a modular unit. By combining hexagonal modular unit of disks in series and in parallel, a wide range of surge arrester could be possible to be constructed. This modular concept could tremendously reduce the cost of production as a standard production line could be possible to be made avoiding setups at various points of the lengthy processing line. The adverse effect arising from the bottom face of conventionally sintered disks cannot be eradicated by removing more materials by grinding. Most of the failures are found to originate from the bottom face. By changing sintering orientation it was possible to lower regrinding rate as well as early failure. Survival of disks above 400 J cm^{-3} was increased by having passivation thickness of $220 \mu\text{m}$. It was also identified that the fracture mechanism in arrester blocks during HASD test is due to stress wave propagation which is the result of injection of high energy within short time. The understanding of the importance of stress wave in this regard should be helpful to effectively combat the situation by adopting appropriate measures. Thus by consolidating all the above mentioned investigative results for the processing of arrester blocks and using appropriate support material in between the disks, a robust surge arrester mechanism can be developed to secure a more reliable electrical system.

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Influence of Nanostructures in Perovskite Solar Cells

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Abbreviations

AFM	Atomic force Microscopy
AM	Air Mass
CdTe	Cadmium Telluride
CIGS	Copper Indium (di) Selenide
CNT	Carbon nanotube
CV	Cyclic Voltammetry
DSSC	Dye-Sensitized Solar Cell
EDS	Electron Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
ETA	Extremely Thin Absorber
ETL	Electron Transporting Layer
ETM	Electron Transporting Material
eV	Electron volt
FESEM	Field Emission Scanning Electron Microscopy
FF	Fill factor
FTO	Fluorine doped tin oxide
GaAs	Gallium Arsenide
GO	Graphene oxide
GQD	Graphene quantum dot
HAXPS	Hard X-Ray Photoelectron Spectroscopy
HOMO	Highest Occupied Molecular Orbital
HRTEM	High Resolution Transmission Electron Microscopy
HTM	Hole Transporting Material
IEA	International Energy Agency
IPCE	Incident Photon to Current conversion Efficiency
I _{sc}	Short-circuit current
ITO	Indium doped tin oxide
LUMO	Lowest Unoccupied Molecular Orbital
MWNT	Multi-walled carbon nanotube
P3HT	Poly-3-hexyl thiophene
PCBM	Phenyl C ₆₁ -butyric acid methyl ester
PCE	Power Conversion Efficiency
PEDOT/PSS	Poly-(2, 3-dihydrothieno-1, 4-dioxin)-poly (styrene sulfonate)
PSC	Perovskite Solar Cell
PTAA	Poly-triaryl amine
QDSSC	Quantum Dot-Sensitized Solar Cell
RGO	Reduced graphene oxide
SAED	Selected Area Electron Diffraction
Spiro-OMeTAD	Spiro-OMeTAD 2, 2', 7, 7'-tetrakis-(N, N-di-4- methoxyphenylamino)-9, 9'- Spirobiflourene
SWNT	Single-walled carbon nanotube
UPS	Ultraviolet Photoelectron Spectroscopy
V _{oc}	Open-circuit voltage
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Introduction

World total annual consumption of all forms of energy increased more than ten-fold during the twentieth century, and in the year 2011, the energy production and consumption were pitched at 518.546 and 520.272 Quadrillion Btu, respectively. This increased to 537.266 and 524.076 Quadrillion Btu respectively, in 2012, as estimated by the International Energy Agency (IEA)¹. The non-renewable energy resources such as coal, oil, and gas have several significant and harmful impacts on the environment that contributes to climate change, hence, the urgent need for the usage of clean and renewable energy sources such as solar power, wind, water, tidal, and geothermal energies. Renewable energy technology, in particular solar photovoltaics, has been viewed as an alternative technology for the past couple of decades. The ever-increasing demand for energy and predicted exhaustion of the non-renewable sources, like fossil fuels, by the end of the century has urged researchers to develop solar power as a clean and abundant form of energy. The total global energy contribution from photovoltaics was <1% in 2013 and it is forecast to increase to ~16% by 2050². However, the widely accepted silicon technology has inherent unsolved challenges that are restricted by material properties with the predicted theoretical efficiency of 33% and as a result the efficiency of these systems are limited by the source material. Although, there has been considerable research and development in the silicon solar cells over the past decades but its efficiency is barely incremental. In order to meet the world energy demands rising up to 2020 and beyond, researchers are looking for disruptive alternative technology to the conventional silicon photovoltaics.

Solar cells are, in general, categorized into different generations based on the materials required for synthesis, applications, and the commercial perspective. First generation silicon technology currently dominates the world photovoltaic market claiming ~90% of the installation. The best laboratory record power conversion efficiency (PCE) for silicon solar cells is ~25% (Green *et al.*, 2012) for single solar cells and ~22% for modules, with the performance being largely dependent on the quality of silicon used. These devices are reliable as well as robust in nature. But they suffer from the drawbacks of high cost of production as well as implementation into solar modules and the theoretical Shockley Queisser limit of efficiency.

Second generation solar cells involve primarily amorphous and thin-film technology such as amorphous silicon, gallium arsenide (GaAs), cadmium telluride (CdTe), copper indium (di) selenide (CIGS) with performance ~20% (NREL, 2015), and lower production costs. The vacuum-based complex processes for materials processing and high temperature treatments for the fabrication of second generation solar cells, more importantly the availability of materials and hence the cost, make them less attractive for large-scale production purposes. However, second generation thin-film solar cells have a niche market in certain industries such as flexible electronics applications.

From the first to the second generation solar cells, the reduction in cost of modules, is a step toward the right direction but the costs are not yet low enough for substantial commercial uptake by consumers as a result of inherent issues with those devices. Third generation solar cells which are based on nanostructured materials from low-cost manufacturing techniques, have attracted more attention due to simplified fabrication process, availability of materials and hence are cost competitive. This motivated various research communities to develop solutions that will ultimately address not only the key challenges on materials availability but also be inexpensive and have high efficiency. Third generation solar cells consists of different types of solar cells such as dye-sensitized solar cells (DSSCs), organic solar cells including polymer devices, quantum dot-sensitized solar cells (QDSSCs), perovskites, and multi-layer tandem devices with amorphous silicon or GaAs. One of the prime candidates with a vertical increase in the efficiency is the recently explored perovskite materials which have emerged as a promising alternative due to their cost effectiveness and high efficiency.

Perovskite solar cells (PSCs) are relatively a new technology, which has currently generated enormous interest owing to their multitude of fascinating properties and the prospect of a low-cost viable alternative to silicon. PSCs along with 2-dimensional nanostructures push the science and technology beyond the era of silicon, bringing these materials and their challenges from academy to industry and hence, society. Only recently, intense research in this field has enabled the efficiency of these devices to improve beyond 20% within a span of few years. Unfortunately, the commercialization of these systems is still some way off because of the inherent challenges associated with the organic molecules in these hybrid perovskite devices.

The development of PSCs is gaining ground along with the conventional solar cell technologies of crystalline and amorphous silicon, as well as the emerging organic photovoltaic systems. This is largely due to their unique properties, low-cost processes of fabrication and the ease of availability of organic-inorganic hybrid materials necessary for their synthesis. The concept of incorporation of perovskites as a sensitizer has emerged from the field of DSSCs (Grätzel, 2003; Upadhyaya *et al.*, 2013) where a light-absorbing dye adsorbed on the surface of a mesoporous n-type conductor and filled-up with a redox electrolyte, functions efficiently as a solar cell. The motivation to find more effective absorbers capable of harnessing a large part of the solar spectrum in thin films, led Miyasaka (Kojima *et al.*, 2006) and co-researchers to investigate the first perovskite-sensitized solar cells. These far-from-optimized devices have seen the incorporation of many modifications to enhance their performance. One such modification being the use of various nanostructures like nanoparticles, nanorods, columnar nanoparticles, and nanosheets which are composed of different materials such as titanium, zinc, tin, aluminum, zirconium, or nickel. These are used to form mesoporous scaffolds or for hole transporters, electron selective contacts and interlayers between perovskite absorber and other layers in the photovoltaic devices. These nanostructured materials help to increase the area of contact between interfaces, thus aiding efficient charge accumulation and separation.

¹International Energy Agency (IEA) Report.

²International Energy Agency (IEA) Report: Technology Roadmap Solar Photovoltaic Energy, 2014 edition (International Energy Agency report 2014).

Nanostructured solar cells show great promise toward new approaches for converting solar energy into electricity. These materials address some of the key challenges in improving the overall efficiency of solar cells. They have excellent surface-to-volume ratios and surface energy for efficient sunlight absorption and effective changes in optical and electronic properties of PSCs. Now-a-days carbon-based nanostructures like graphene (You *et al.*, 2015; Wang *et al.*, 2014a), graphene-oxide (GO) (Wu *et al.*, 2014; Li *et al.*, 2014a), carbon nanotubes (CNTs) (Li *et al.*, 2014b; Habisreutinger *et al.*, 2014b; Wang *et al.*, 2014b), graphene quantum dots (GQDs) are being used to replace conventional hole-transporting materials (HTMs) and metallic counter electrodes, which not only require expensive deposition techniques but also interfere with device stability and involve complicated vacuum deposited noble metal electrodes.

Historical Overview

Nanoscale structures provide ample opportunities to revolutionize the conversion of solar energy by enabling highly efficient and low-cost devices. Nanoscale systems exhibit various properties that are vastly different from bulk or thin-films of the same compounds, and have allowed new ways of solar energy conversion for electricity generation. The large surface-to-volume ratio of nanomaterials can have varied benefits, and, moreover, objects with sizes in nano regime can also exhibit quantization effects, which becomes more pronounced with decreasing size. Reflection losses from the front surface of solar cells is a persistent problem with solar cells. Nanostructured surfaces can help in reducing such reflection losses when the size of the nanostructures is smaller than the wavelength of the incident light. If those nanostructures are also used as the active components, then the need of costly anti-reflection coatings and texturing can be dispensed with. Furthermore, patterned nanostructures can be designed to capture even more sunlight via light trapping. Incorporation of nanoparticles in photovoltaics involves significant reduction in material usage and associated final costs. In addition, these photovoltaic devices are not bound by the theoretical limiting efficiency values. PSCs have seen the utilization of several such nanostructures as sensitizer, hole and electron transporter, and as interlayers. The interest in organic-inorganic hybrid halide perovskite is almost a century old (Green *et al.*, 2014; Topsøe, 1884) but was not pursued consistently owing to toxicity issues with lead (Pb) and partly because other materials, like tin (Sn), were not considered robust enough. The methylammonium lead trihalide ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X}=\text{I}, \text{Br}, \text{Cl}$) perovskite has come to the forefront of photovoltaic research since the pioneering work by Miyasaka *et al.*, proposing a new direction for DSSC fabrication. The first work in 2006 with methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) was reported with an efficiency value of 2.2% and in 2009 using methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) as the sensitizer in a liquid DSSC resulted in PCE of 3.8%, although the device's long-term stability remained an issue. This poor stability was due to the dissolution of the perovskite in the electrolyte. This bottleneck was largely overcome by the fabrication of solid-state DSSCs. In 2012, Park, Grätzel *et al.* fabricated DSSCs by replacing the liquid electrolyte with solid HTM, spiro-OMeTAD (2,2',7,7'-tetrakis (N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene) and reported a PCE of 9.7%. The real breakthrough in PSC research came with the incorporation of several novel approaches by Henry Snaith and his group (Lee *et al.*, 2012) which improved the efficiency of perovskite devices to 10.9%. One of these developments was the usage of mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. A second involved coating nanoporous TiO_2 surfaces with a thin perovskite layer, thereby forming extremely thin absorber (ETA) cells. The third was replacing conducting nanoporous titania (TiO_2) by a similar but non-conducting alumina (Al_2O_3) network. And, fourth was deployment of simple planar cells with the scaffolding completely eliminated, thus proving the ambipolar nature of PSCs. Seok *et al.* reported a further jump in efficiency to 12% by implementing a solid perovskite capping layer over the mesoporous scaffold. They also improved the efficiency to 12.3% by using mixed halide perovskites $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$. In 2013, Grätzel's group used TiO_2 scaffolding and two-step iodide deposition and reported an efficiency improvement to over 15%. Snaith's group reported planar PSCs without scaffolding with efficiency value of 15.4%. At the end of 2013, Seok's group achieved an efficiency of 16.2% by using the mixed-halide $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ and poly-triaryl amine (PTAA) as HTM (Green *et al.*, 2014). The latest record is set at 20.1% (NREL, 2015) by the Korea Research Institute of Chemical Technology in November 2014 which marked a fivefold increase in efficiency since its inception just three years earlier. Thus research on perovskite materials has ignited the mind of researches and it is a disruptive technology considering it is less than a decade old when compared to the decade-long developments of silicon technology.

The excellent tunable properties of ambipolar (i.e., both p- and n- conductive) charge transport (Giorgi and Yamashita, 2015), high charge carrier mobilities, long diffusion lengths (Stranks *et al.*, 2013), and high open circuit voltages (Ryu *et al.*, 2014) make these materials as a suitable alternative to silicon-based devices. Easy and low-cost methods of fabrication of these materials include spin-coating, drop-casting, screen printing, and doctor blading. Reference for large-scale manufacture, roll-to-roll printing provides optimism toward the wide use of perovskite materials for solar cell fabrication.

The materials currently used are organic-inorganic hybrid materials such as methylammonium lead trihalides and ethyl ammonium lead trihalides. Formamidinium lead halide is another perovskite which has a potential to develop larger interest because of its suitable band gap which is tunable between 1.48 to 2.23 eV (Eperon *et al.*, 2014; Lee *et al.*, 2014; Pellet *et al.*, 2014) for harnessing a larger amount of the solar spectrum compared to methylammonium devices which have a band gap 1.55 eV and greater. This results in higher efficiency and it has greater stability (Aharon *et al.*, 2014) when compared to methylammonium lead halide devices. Devices with larger size cations compared to CH_3NH_3^+ (such as $\text{CH}_3\text{CH}_2\text{NH}_3^+$ and $\text{NH}_2\text{CH}=\text{NH}_2^+$) increase the t factor and push the perovskite crystal structure toward its symmetrical cubic phase. Different proportions of organic cations, inorganic cations, and halide ions have been incorporated in mixed perovskites. Several types of HTMs/hole transporting layers (HTLs) and electron transporting layers (ETLs) have also been used.

Different layers of a PSC are formed from nanostructures with the meso-superstructured solar cells having a mesoporous layer of titania or alumina as scaffold, the ETL, the HTM, the perovskite layer, and the counter electrode being composed of nanos-

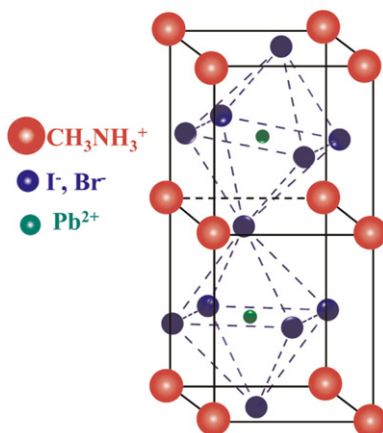


Fig. 1 General perovskite crystal structure.

structures. Carbon and nanostructured carbon-based materials are being probed and incorporated into perovskite devices in place of the other HTMs like spiro-OMeTAD. This is because such materials are not only expensive, hence limiting the possibility of their usage in large-scale fabrication, but also because they may prove to be detrimental to the stability of perovskite devices. As a consequence, graphene, graphene oxide (GO), reduced graphene oxide (RGO), CNTs, fullerenes, GQD, and sheets of graphite are being currently used as HTM, ETL, blocking layer, and counter electrodes in PSCs. Also, they are often used as interlayers for enhancing the performance of devices. The details about the different nanostructures will be discussed in later sections.

The purpose of this article is to discuss about the role of various types of nanostructures used in the different layers of PSCs. This article aims to give an overview of the perovskite materials, mechanism of operation of PSCs, fabrication procedures and their different architectures, followed by the influence of nanostructures in these systems. The 2-dimensional (2D) materials such as graphene and nanocarbons, capable of causing breakthrough achievements, will also be reviewed as well as the inherent challenges associated with perovskite devices. We will focus primarily on the oxide and carbonaceous nanostructures/nanoparticles.

What are Perovskites?

Perovskites are a mineral of calcium titanium oxide CaTiO_3 named after the Russian mineralogist Lev Perovski. In practice all crystals having structures of the form AMX_3 are classified as perovskite materials. The ideal perovskite crystal structure is cubic with A and M being two cations (as shown in Fig. 1). Fig. 1 shows the methylammonium lead trihalide PSC where methylammonium ion is the A cation. M is a divalent cation and X is an anion. The perovskite materials most widely used are organic-inorganic hybrid in nature, with A being any organic species mostly methylammonium cation $[\text{CH}_3\text{NH}_3^+]$, ethylammonium or formamidinium cation $[(\text{NH}_2)_2\text{CH}^+]$, M being a cation [lead (Pb^{2+})/tin (Sn^{2+})] and X a halide ion, chlorine (Cl), bromine (Br), or iodine (I). The crystal structure of perovskite materials are as shown in Fig. 1. Perovskite materials are observed in cubic, tetragonal, or orthorhombic crystal structures. The ideal cubic crystal structure of perovskite materials often get distorted or tilted into less symmetric tetragonal or orthorhombic structures. This depends on the size of the A cation which according to the Goldschmidt tolerance factor as given in Eq. (1)

$$t = \frac{r_B + r_X}{r_A + r_X} \quad (1)$$

where r_A = radius of A cation, r_B = radius of B cation, and r_X = radius of X anion, determines the stability and distortions of the crystal structure. Cation A can have a very limited size in the crystal lattice. A value of t between 0.9 and 1 gives the ideal cubic perovskite structure whereas any other value denotes tetragonal or orthorhombic crystal structure. The alteration in the size of the cation can lead to distortions in the crystal lattice and whether the distortions and defects are beneficial or detrimental for the PSC is still open to debate. This has led to an exciting area of research and technological development.

Structure of Perovskite Solar Cells

An archetypal PSC comprises an n-type compact layer, a mesoporous oxide layer, a light-harvesting perovskite layer, a hole-transporting layer and two electrodes. The generic structure of a PSC is as shown in Fig. 2 and the different layers are deposited as indicated stepwise.

Step 1: The Fluorine doped Tin Oxide (FTO)/Indium doped Tin Oxide (ITO) coated glass, acts as the substrate for the photoanode of the perovskite device.

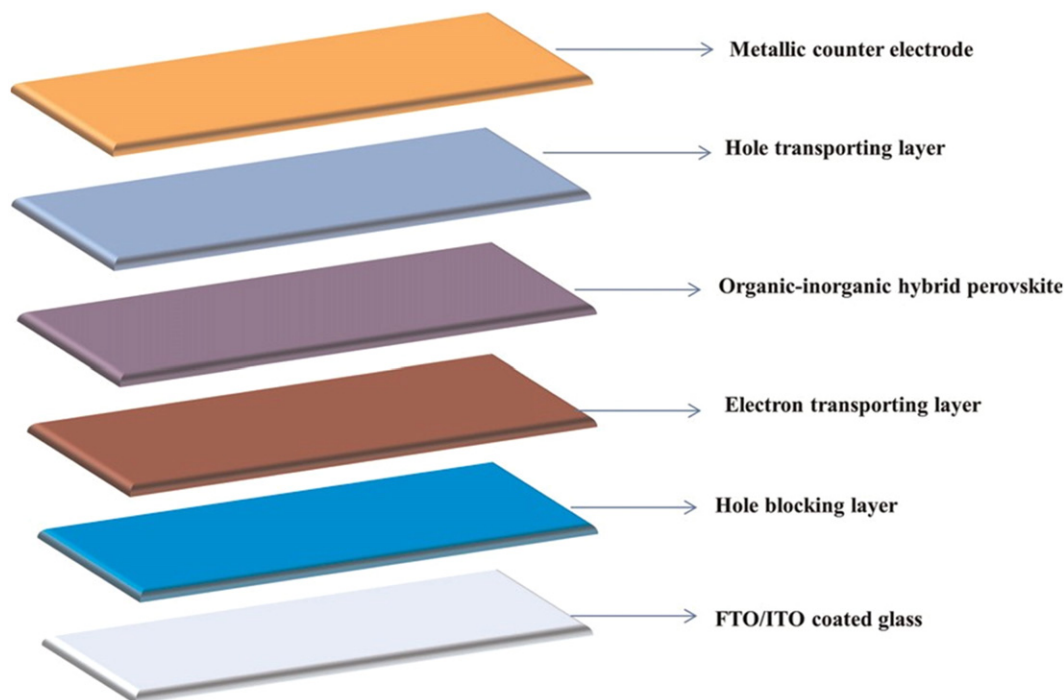


Fig. 2 Generic structure of perovskite solar cells.

Step 2: Above it there is a dense layer of semiconducting material primarily TiO_2 which functions as the hole blocking layer or compact layer, deposited usually by spin-coating or spray-coating on top of the FTO substrate. It prevents the holes extracted by the electron selective layer above from coming into contact with the FTO/ITO glass and inhibits recombination losses.

Step 3: Next is the ETL which facilitates diffusion of the electrons from the photoexcited perovskite layer into the FTO/ITO glass and thus to the external circuit. Materials most commonly used as ETLs are titania (TiO_2), tin oxide (SnO_2), zinc oxide (ZnO), and nickel oxide (NiO). Carbon based materials like graphene, GO, RGO, CNTs, GQDs, and (6, 6)-phenyl C_{61} -butyric acid methyl ester (PCBM) are also being suitably utilized for electron transport operations in PSCs (Wang *et al.*, 2013; Li *et al.*, 2014a; Yeo *et al.*, 2015; Habisreutinger *et al.*, 2014b).

Step 4: The perovskite layer which can act either as sensitizer or absorber or as electron or hole transporter, although its primary function is that of a sensitizer, is spin-coated over the electron transporting layer.

Step 5: Adjacent to the perovskite layer is the hole transport layer (HTL) which allows the holes from the excited perovskite to move toward the metallic cathode for extraction. The commonly used hole transporters are 2, 2', 7, 7'-tetrakis (N, N-di-p-methoxy phenylamine)-9, 9'-spirobifluorene (spiro-OMeTAD), poly-3-hexyl thiophene (P3HT), poly-triaryl amine (PTAA), and poly-(2, 3-dihydrothieno-1, 4-dioxin)-poly (styrene sulfonate) (PEDOT/PSS). Carbonaceous nanostructures of graphene, GO, and CNTs are currently being used to replace the aforementioned expensive and degradation-prone HTMs.

Step 6: Finally, there is a metallic contact layer which is usually deposited by thermal vaporization on top of the solar cell to function as the counter electrode, also known as back contact. This layer is usually any noble metal such as Au or Ag, often Al. But these noble metal cathodes require high temperature sintering and vapor deposition as an essential part of fabrication, thus increasing production cost. Carbon, CNTs, and graphene are often used to circumvent the expensive techniques and fabricate transparent counter electrode.

General Working Principle of Perovskite Solar Cells

The working principle of a PSC is as described in Fig. 3. The different layers are carefully chosen to optimize the efficiency of PSCs. Energy levels of the different materials in the solar cells must be so chosen that they are well aligned and thermodynamically suitable for good device performance. The perovskite layer absorbs sunlight and the energy in a photon is used to excite an electron. This absorption is manifested as an electron being excited from the valence band edge (or highest occupied molecular orbital, HOMO) of the perovskite sensitizer to its conduction band edge (or lowest unoccupied molecular orbital, LUMO) leaving the perovskite in an oxidized state which is neutralized by an electron moving from the HOMO of the adjacent hole transporting layer. The electron excited to the LUMO of the perovskite is then injected into the LUMO of the ETL and is transported via diffusion to the front contact. The energy levels are thermodynamically aligned in such a way that when an electron from valence band edge of the perovskite is excited to conduction band edge, it leaves behind a hole in the perovskite, then another electron

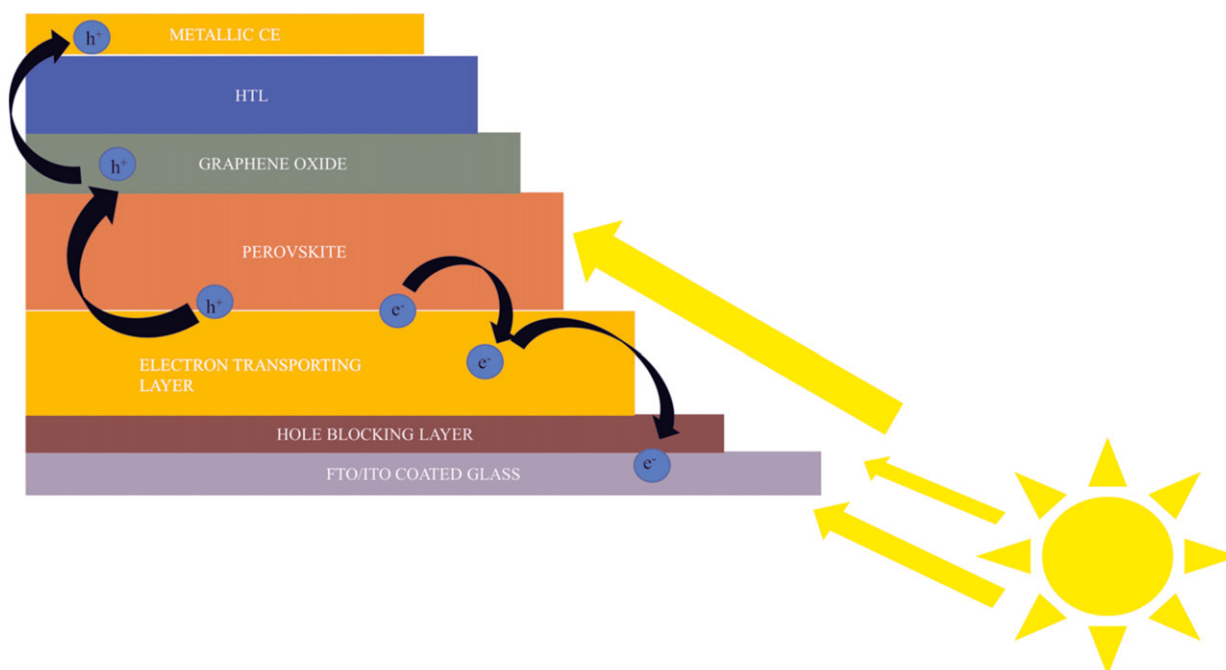


Fig. 3 General working principle of perovskite solar cells.

from the HOMO of the HTL can fill up its place. Thus by the movement of electrons and holes in a hopping manner, an electric current is generated. The HTL allows the holes extracted from the perovskite layer to pass through and they are extracted into the external circuit. The HTL also functions as an electron blocking layer and prevents any electron from passing through. The important function of electron-hole charge separation thus occurs at the interfaces of different layers and the electrons and holes are transported through electron and hole selective conductor layers respectively.

For efficient power output, the band gap of the perovskite absorber should be sufficient to absorb visible light. The optimal band gap for a single junction solar cell is between 1.1 and 1.4 eV. The conduction band edge of the perovskite absorber should be slightly higher than the conduction band energy of the electron transporter, so that transfer of photoexcited electrons is energetically favorable. Similarly, the valence band edge of the perovskite layer should be slightly lower than that of the hole conductor to allow proper hopping of holes.

Different Architectures of Perovskite Solar Cells

PSCs are used in many different architectures primarily as sensitizer, meso- superstructured, planar heterojunction, and hole conductor-free architecture as shown in **Fig. 4**. Sometimes the perovskites are also fabricated in inverted architecture. In the sensitizer approach, the perovskite layer behaves primarily as an absorber layer, absorbing sunlight, which excites electrons from the HOMO to the LUMO of the perovskite layer.

In meso-superstructured solar cells (MSSCs) there is a layer of mesoporous semiconducting oxide, such as titania (TiO_2) or alumina (Al_2O_3), which acts as a scaffold and prevents recombination of electron-hole pairs. Because of the presence of the mesoporous oxide layer, these types of perovskite devices are referred to as MSSCs. The mesoporous scaffold in these devices prevents the diffusion of the electrons through them. Electrons are forced to reside in the perovskite itself which then facilitates electron transport, proving its ability as a sensitizer as well as n-type conductor. Al_2O_3 is an insulator with a wide band gap of 7 to 9 eV (Lee *et al.*, 2012) which is observed to be a more suitable mesoporous scaffold than TiO_2 , because electron transfer through perovskites is much faster than through TiO_2 and there is an improvement in the open circuit voltage (V_{OC}), hence also PCE.

PSCs are also used in planar heterojunction architecture where different layers like ETL, perovskite sensitizer, HTM, and cathode are deposited in the form of thin films. In the p-i-n heterojunction solar cell approach, perovskite semiconductors perform all the functions of photovoltaic systems, light absorption, charge generation, and transport of both types of charges, electrons, and holes. The perovskites can also be used in hole-conductor free approach where the perovskite layer not only behaves as the sensitizer but due to its ambipolar nature also extracts the holes and allows their passage so that the utilization of the HTL can be dispensed with. This type of PSC is known as 'hole conductor-free' architecture.

Often, PSCs are deposited with the HTM on top of the FTO/ITO coated glass followed by the perovskite layer, the ETL and the metallic counter electrode which is known as the inverted architecture.

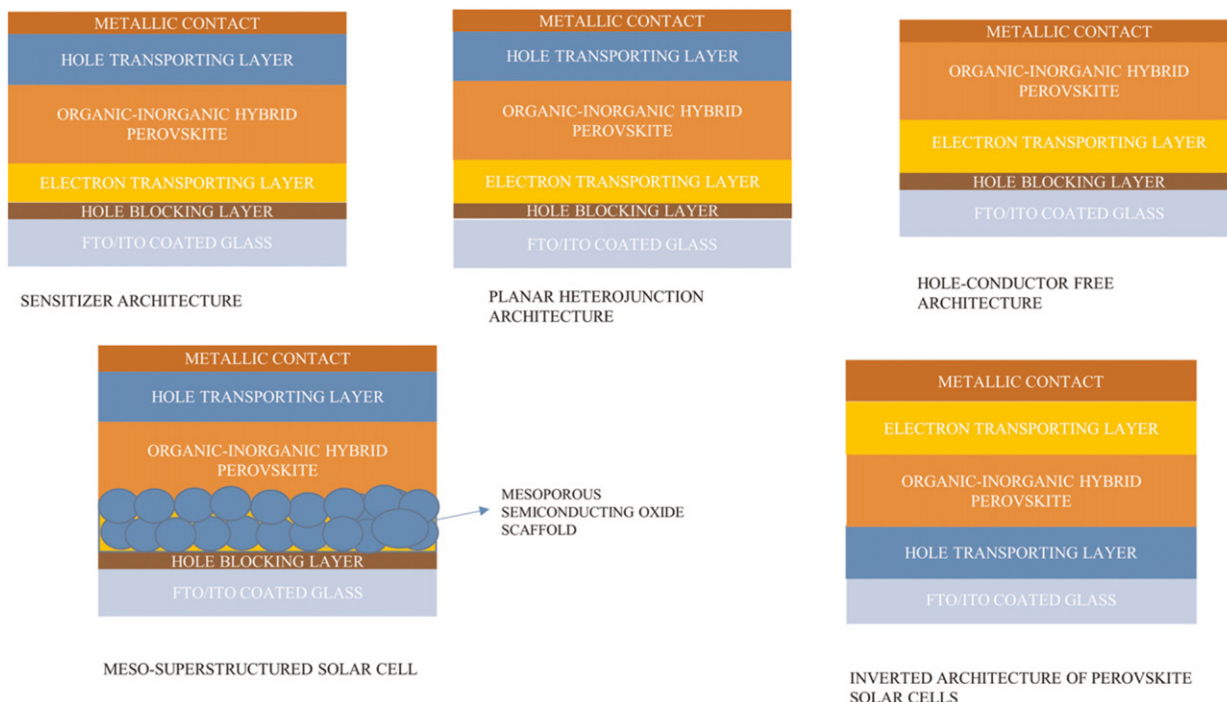


Fig. 4 Different architectures of perovskite solar cells.

Influence of Nanostructures in Perovskite Solar Cells

Any structure, particle, mesh, fiber, rod, tube, ribbon, film, or sheet, which falls in the nano regime i.e., has at least one dimension within 1 and 100 nm, is known as a nanostructure. They can be classified into one dimensional nanostructured surfaces, two dimensional nanotubes or three dimensional nanoparticles. Nanostructures have received steadily growing interest as a result of their unique properties and applications which are far superior to their bulk counterparts. Nanostructuring is an effective and versatile means of modifying the electrical, optical, and magnetic properties of any material. Nanoparticles have excellent surface-to-volume ratios, thus offering high surface area for efficient charge accumulation, transport, and interface wettability along with the tunable electronic and optical properties of PSCs. In the next section we will discuss the different oxide and carbonaceous nanostructures which have varied applications in the different layers of PSCs.

TiO₂

Titania/titanium dioxide (TiO₂) is the most commonly used ETM in PSCs. Size, morphology, and crystal structure determine the physical and chemical properties of nano TiO₂. Titania exists in three different phases namely rutile, anatase and brookite, with the rutile phase being thermodynamically most stable. Anatase is considered to be the most suitable phase for photocatalytic activity and solar-energy applications. It is well known that nanostructures of TiO₂ such as nanorods, nanowires, and nanotubes (as shown in Fig. 5(A)) play prominent roles in functional devices due to their dimensionality and quantum confinement effects. The thickness of the nanoporous layer of TiO₂ is important in determining the solar cell performance. Charge collection and electron transport in PSCs are dependent on the morphology, porosity, surface area, and size of the TiO₂ layer. In meso- superstructured devices, mesoporous titania and alumina are used as insulating scaffold as shown in Fig. 5(B). Mesoporous particles are those having sizes between 2 and 50 nm. Titania has a band gap of 3.2 eV in anatase phase and 3.03 eV for rutile phase (Scanlon *et al.*, 2013). This band gap is suitable for the transport of electrons and holes through the PSC. But the deposition of titania requires high temperature sintering at 400–500 °C which makes it unsuitable for usage on plastic substrates. Hence, ZnO with comparable energy level, good electron transport properties and feasibility of electrodepositing is a viable alternative. In addition to mesoporous TiO₂ films, a variety of materials are also used in PSCs as ETM and scaffold such as one-dimensional TiO₂ nanowires, rutile TiO₂ nanorods, ZnO nanorods, [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM), Al₂O₃, and ZrO₂.

Al₂O₃

Alumina is successfully used as an insulating scaffold for the perovskite absorber layer in MSSCs and it can be fabricated at low-temperatures of 150 °C. The band gap of alumina (~ 7 to 9 eV) is higher than that of the LUMO of the perovskite, so it does not

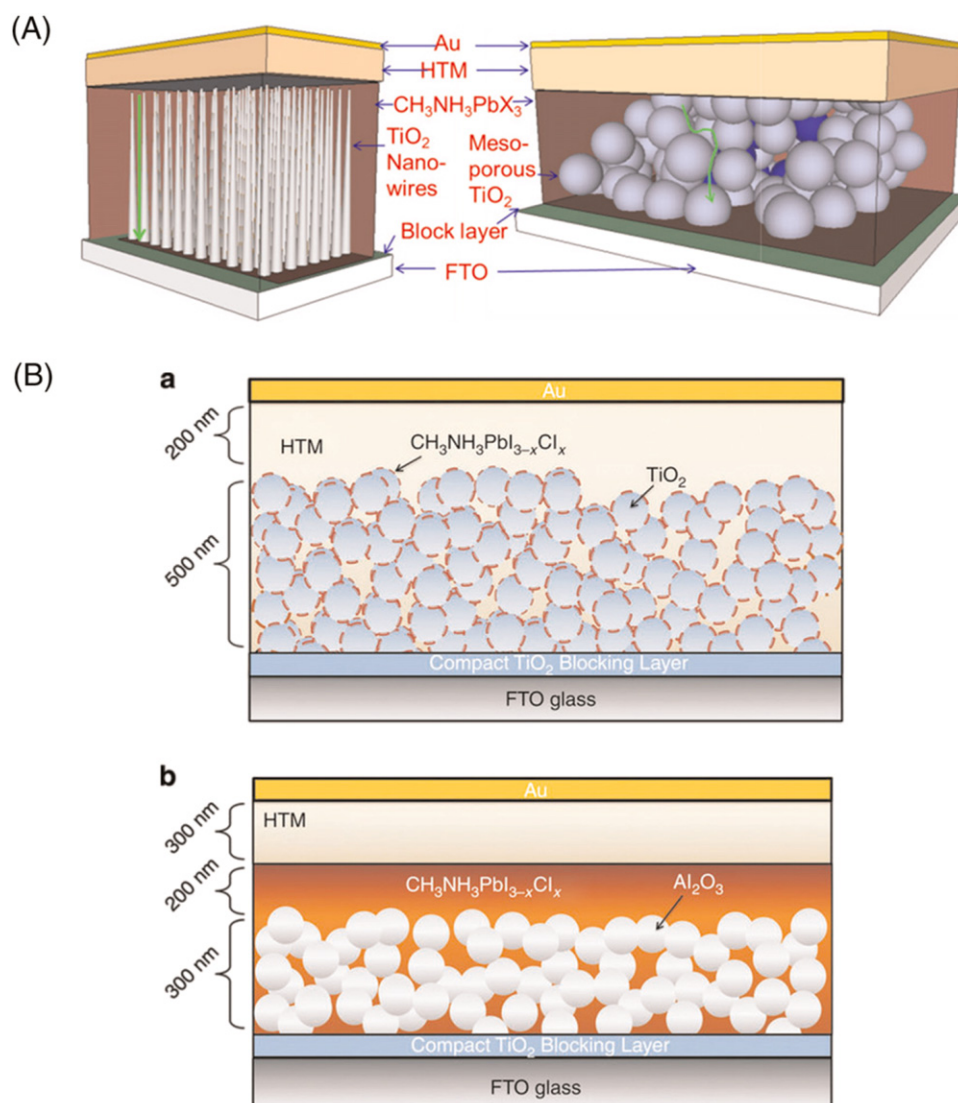


Fig. 5 (A) Nano-wires of TiO₂ and TiO₂ as mesoporous scaffold used in perovskite solar cells. Reproduced from (Jiang *et al.*, 2014) with permission of The Royal Society of Chemistry. (B): (a) TiO₂ and (b) Al₂O₃ mesoporous scaffolding in perovskite solar cells. Reprinted by permission from Macmillan Publishers Ltd: [Nature Communications] (Leijtens *et al.*, 2013) copyright (2013).

allow the excited electrons to diffuse into the alumina scaffold and the extraction of electrons is facilitated only by the perovskite layer due to its ambipolar nature as depicted in Fig. 6. The figure shows a comparison of the mechanism of electron-hole movement through mesoporous TiO₂ and Al₂O₃. The red cross in the band diagram for Al₂O₃ implies that the photoexcited electrons from the conduction band of the perovskite cannot hop to the conduction band of alumina scaffold due to the higher band edge position. The alumina layer acts as a barrier and prevents charge recombination.

SnO₂

Traditional mesoporous TiO₂ layer is also replaced with mesoporous SnO₂ nanoparticle film as ETL and scaffold. The SnO₂ layer treated with TiCl₄ results in reduced charge carrier recombination at the interfaces. SnO₂ has a higher conduction band as compared to TiO₂ and should facilitate a more efficient transfer of photo-generated electrons as compared to TiO₂. Moreover, the higher electron mobility of SnO₂ compared to TiO₂ is also expected to make it a versatile material for use as ETL. But the devices with SnO₂ suffer from the drawback of recombination between SnO₂ and HTM. Passivating the surface of the SnO₂ nanoparticles with an aqueous solution of TiCl₄ (Li *et al.*, 2015) or wide band gap insulating oxides, such as MgO or Al₂O₃, results in suppression of the backward reaction and enables a significant enhancement in the PCE by retarding charge recombination by avoiding internal trap states and facilitating electron transport from perovskite to the SnO₂ conduction band. There is an optimum film thickness above which, if the SnO₂ film thickness increases, the PCE decreases as the charge carriers have to travel further, distance thus increasing the probability of recombination.

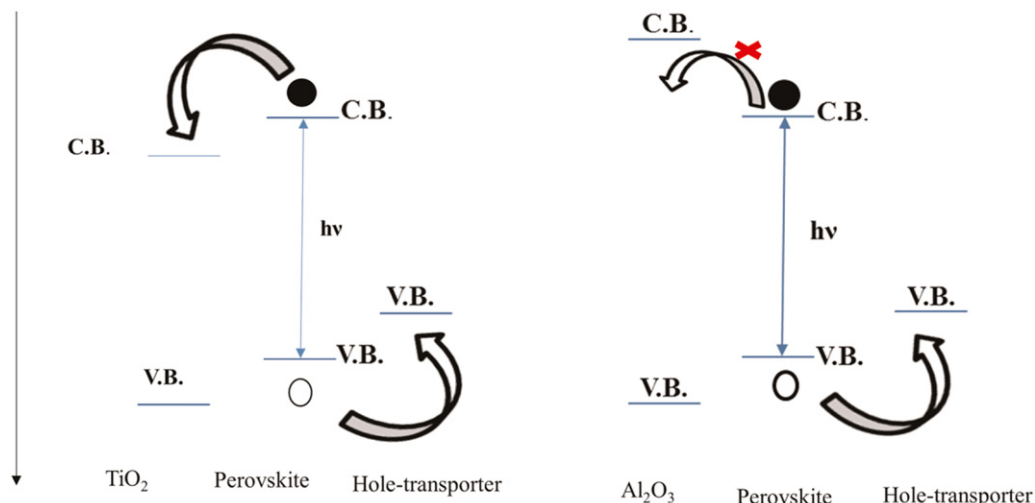


Fig. 6 Band alignment and mechanism of electron-hole movement through TiO_2 and Al_2O_3 mesoporous perovskite solar cells. Adapted version of Fig. 3(A) from Lee, M.M., Teuscher, J., Miyasaka, T., Murakami, T.N., Snaith, H.J., 2012. Efficient hybrid solar cells based on meso-structured organometal halide perovskites. *Science* 338, 643.

ZnO as Electron Extracting Layer

Zinc oxide (ZnO) is an n-type, direct, wide band gap, semiconductor material (3.37 eV at 300 K) which can be grown by various techniques with good structural quality at low-temperature and with its conductivity being several orders of magnitude higher than that of TiO_2 , it favors electron transport toward the front contact. Hence, ZnO is often used as an alternative ETL to TiO_2 and in order to improve PCE, low-temperature hydrothermally processed double-layer of ZnO nanostructures have also been implemented in PSCs. Unlike mesoporous TiO_2 , the ZnO layer is substantially thinner and does not require sintering as an essential part of fabrication because there are various deposition techniques, namely solution-processed methods, plasma-enhanced chemical vapor deposition and, electrochemical deposition which can be used for improving the device performance of PSCs. Several different structures of ZnO, ranging from arrays of nanowires and, nanorods to compact thin films, have also been employed. But charge recombination often occurs at the ZnO/absorber interface deteriorating solar cell performance. This deterioration can be addressed by using interfacial modifications with nanostructures. Aluminum doped ZnO nanorods (Dong *et al.*, 2014) are more suitable options to retard charge recombination at the ZnO/perovskite interface because they have a higher conduction band, faster electron mobility, and higher electron density compared to ZnO with maximum efficiency reaching 10.7%. Nanorods grown perpendicularly onto various substrates in the form of densely packed assemblies with a high surface-to-volume ratio are suitable candidates for hybrid photovoltaic systems because they function as an efficient charge collection system.

ZrO_2 as Scaffold

A double layer of mesoporous TiO_2 and ZrO_2 as a scaffold infiltrated with a perovskite layer has also been used in a hole-conductor free PSC. This acts as a barrier between the photoanode and the carbon counter electrode avoiding direct contact between the two (Mei *et al.*, 2014). The conduction band edge of TiO_2 is at -4 eV while that of ZrO_2 is at -3.4 eV (energy levels measured with respect to vacuum) and hence any electron from the photo-excited perovskite injected into the TiO_2 layer is not allowed to move to the back contact due to the 0.6 eV energy difference with the ZrO_2 layer. ZrO_2 prevents the photogenerated electrons from moving to the back contact, thus preventing recombination with the holes from the perovskite at the back contact.

NiO

Nickel oxide (NiO) is an intrinsic p-type semiconductor with a wide band gap and good thermal and chemical stability. NiO has been employed as photocathode material in p-type DSSCs, tandem DSSCs and as a hole collector in organic bulk heterojunction and perovskite heterojunction solar cells. NiO functions as an interfacial layer as well as electron blocking material because of its higher conduction band compared to $\text{CH}_3\text{NH}_3\text{PbI}_3$ (-1.8 eV vs. -3.93 eV) (Liu *et al.*, 2015). Introduction of NiO is seen to extend the electron lifetime and enhance the hole extraction by the counter electrode.

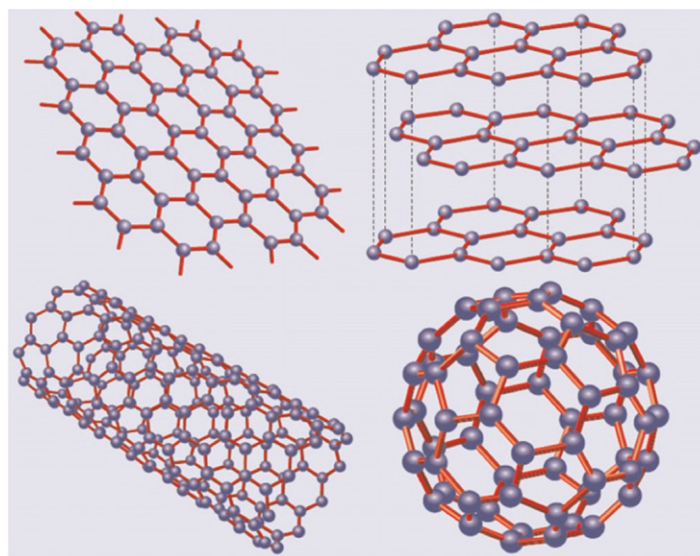


Fig. 7 Different nanostructures of carbon: graphene, graphite, fullerene, and carbon nanotube. From top left, clockwise) (Castro Neto *et al.*, 2009).

Carbon

Different nanostructured carbonaceous materials (as shown in Fig. 7) such as graphene, GO, RGO, CNTs, fullerenes and GQDs find applications as electron transporters/hole transporters, interlayer between perovskite and hole selective contact, as blocking (compact) layer as well as counter electrodes in perovskite photovoltaic devices. Graphene is a two-dimensional honeycomb lattice where carbon is sp^2 hybridized. It is the parent material for the formation of CNTs and fullerene. Graphene is currently of much interest owing to its excellent mechanical, electronic properties and its immense potential in nanoelectronic applications. This allotrope of carbon is not only an excellent electrical conductor at room temperature, but also finds use in next-generation transistors, transparent electrodes in solar cells, and many other applications. Graphene can be easily produced via the reduction of GO. It offers tremendous opportunities for functionalized materials. Carbon allotropes having cylindrical structures are known as CNTs. They are one dimensional in nature. They are hollow structures with walls formed of one-atom-thick sheets of carbon, graphene. The graphene sheets rolled at specific angles form the nanotubes. Nanotubes are categorized as single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). Fullerene is a molecule of carbon in the shape of a hollow sphere, ellipsoid, or tube as well as several other shapes. Carbon-based materials find efficient use in PSCs as mentioned below.

Back Contact

Thin films of noble metals like gold (Au), silver (Ag), often aluminum (Al) prepared by thermal vaporization are frequently used as the back contact in PSCs. However, this process not only involves complicated technology but also is expensive and hence limits large-scale production. Therefore, carbon based nanomaterials have been used to replace the costly counter electrodes because they are low-cost, abundant and possess good chemical stability and conductivity. Carbon, with a valence band edge of -5 eV (Ku *et al.*, 2013), is suitable for receiving holes from the photoexcited perovskite absorber. It is also an effective substitute to the expensive but poor stability HTMs. The interface between perovskite and HTM is important for efficient charge separation and transfer. Ambipolar GO can be used to improve the wettability of the interfacial layer providing good contact between the perovskite and hole selective layer for proper hole extraction and reduced charge recombination (Li *et al.*, 2014a).

Hole Transporting Layer

After photoexcitation of the perovskite absorber, the holes are extracted by the hole selective contact. This is achieved using suitable materials with appropriate band edges which thermodynamically facilitate the process. The most widely used material is the expensive and relatively unstable spiro-OMeTAD. Cheaper alternatives like CNTs or CNT-polymer composites can also being used. The polymer poly-(methyl methacrylate) (PMMA) inhibits moisture ingress and hence prolongs solar cell lifetime (Habibreutinger *et al.*, 2014a). GO as an alternative HTM can be used in PSCs employing a $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ absorber (Wu *et al.*, 2014), the GOs could have their intrinsic disadvantages for HTMs such as an insulating property and a high degree of oxygen

contents on their surfaces. RGO is being used as HTM to obtain highly stable and highly efficient PSC as it fulfills the requirements of an ideal HTM in terms of low-cost, abundance, solution-processability, conductivity, and stability.

Perovskite Absorber Layer

Perovskites are used as sensitizers because of their efficient light-harvesting properties. Nanocarbons like GQD and self-assembled monolayer (C_{60} SAM) can be incorporated into the photoactive layer for efficient light harvesting. The usage of C_{60} SAM results in improved open circuit voltage for the PSC whereas the GQDs serve as a bridge to facilitate electron injection from perovskite to the TiO_2 conduction band.

Blocking (Compact) Layer

The blocking or compact layer is an important part of the PSC because it prevents charge recombination between the FTO and perovskite or FTO and HTM and hence should be uniformly deposited. Crystalline TiO_2 is the best example of such a blocking layer. But its fabrication involves high temperature sintering which in turn results in undesirable increased cost of production. Hence, low-temperature processed graphene/ TiO_2 nanocomposites are employed as blocking layers. These composites also minimize the series resistance of cells and graphene, owing to its excellent conductivity, facilitates rapid electron transfer within the network thus reducing recombination losses. The conduction band edge of graphene is suitably placed at -4.4 eV ([Batmunkh et al., 2015](#)), thus aiding in electron transfer from TiO_2 to FTO without any energy barrier.

Graphene/CNT composites can be used as transparent conductive electrodes. CNT can also be used as a transparent top contact which acts as a hole collecting layer and allows light transmission. Flexible PSCs can be prepared by continuously winding multi-walled carbon nanotube (MWNT) sheets onto a fiber electrode. Graphene is the one of the most suitable candidates for transparent conducting electrode, due to its high transparency, good conductivity, and smooth surface. Graphene can replace the conventional FTO/ITO electrodes due to its mechanical and chemical robustness, excellent optical and electronic properties, and potentially low cost. Graphene/ TiO_2 nanocomposites are used as electron transporting layers in meso-superstructured solar cells, with graphene providing good charge collection. Incorporating nanocarbons into the mesoscopic layer of the PSC can lead to improved device performance.

These nanostructures are used in various forms in the PSCs. Titania and alumina are used as insulating scaffold to hinder movement of electrons through them and force their transport through the perovskite layer itself. This is also useful in reducing recombination loss and improving the stability of the PSC. Carbon nanostructures are being implemented for several different purposes. The first usage of carbonaceous material in PSCs was by Han's group ([Ku et al., 2013](#)) who implemented carbon as counter electrode in perovskite photovoltaic devices and achieved a PCE of 6.64%. GO is being used as a counter electrode as well as an interlayer between perovskite and HTM with reported PCE of $\sim 12\%$ ([You et al., 2015](#)) and 14.5% ([Li et al., 2014a](#)), respectively. CNTs are also used as counter electrodes and [Li et al. \(2014b\)](#) were the first to report on the usage of CNTs as counter electrodes.

General Characterization Techniques for Perovskite Solar Cells

To characterize solar cells, various techniques are used which provide information about the working of different parts of the device. UV-vis spectroscopy measures the absorption characteristics, I-V measurements characterize the overall energy conversion of the solar cell.

Incident Photon to Current conversion Efficiency (IPCE) measures the current generated at each wavelength. IPCE gives information about which solar energies or wavelength that can contribute to the photocurrent. The transport time for the electrons in the solar cell and the electron lifetime in the mesoporous semiconductor can be studied with photocurrent and photovoltage measurements. Field emission scanning electron microscopy (FESEM) is used to image the morphological features of the different layers and cross-section of the solar cells. Electron dispersive spectroscopy (EDS) is used to study and confirm the presence of different elements in the device. Sample purity is determined using X-ray diffraction (XRD). High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) techniques are used to study the structural properties and defects in the device. X-ray photoelectron spectroscopy (XPS) is a suitable method used to perform element specific surface and interfacial studies and distinguish the different elements and the nature of their chemical environment present at the surface of the device, also to undertake depth profiling measurements. Hard X-ray photoelectron spectroscopy (HAXPS) can be used to probe deeper into the device surface up to 20 nm whereas XPS allows only surface studies up to about a few nanometers. Impedance spectroscopy (IS) is a tool for investigating the properties and quality of PSCs and it gives information about the fundamental mechanisms of operation of devices. EIS also investigates the interfacial charge transfer in the perovskite devices. Raman spectroscopy is a powerful, non-invasive tool to study the thickness, doping, strain and thermal conductivity of the PSCs. Atomic force microscopy (AFM) is used to measure and determine the surface roughness of the films in the solar cells. Cyclic Voltammetry (CV) will give information about active area of metal or metal atoms involved in the reactions, the reaction and electron transfer

kinetics. Energy levels are measured with the aid of Ultraviolet Photoelectron Spectroscopy (UPS). The energy conversion efficiency of a solar cell is deduced from an I - V curve. The solar cell is illuminated with a solar simulator with a spectrum of AM1.5. During illumination, the current is measured as a function of the voltage, with the current at 0 V signifying the short-circuit current, I_{SC} and the voltage at 0 current giving the open-circuit voltage, V_{OC} . As power is the product of V and I , it should be actually a square but any deviation from the theoretical maximum of the device is described by the fill factor (FF). The efficiency η is given by

$$\eta = \frac{I_{SC}V_{OC}FF}{P_{in}} \quad (2)$$

where P_{in} is the light intensity in mW cm^{-2} . Eq. (2) is used to calculate the efficiency of solar cells.

Several different characterization techniques are also undertaken to show the impact of the nanostructures on the PSCs.

Challenges and Problems with Perovskite Solar Cells

Though perovskite materials show promising results in terms of improvement in efficiency, they do suffer from some drawbacks which have retarded their commercialization. Since, they are formed of organic cations, they are susceptible to moisture, temperature, UV radiation, and oxygen thus deteriorating the performance of solar cells. Moreover, PSCs fabricated by the relatively easy and cost-effective solution processed technologies are prone to inherent imperfections and defects which in turn lead to recombination of charge carriers which is detrimental to solar cell performance. Hence, current research is focused on fabrication of efficient but stable solar cells. The reliability of these solar cells is not very good because of their stability issues. But research is being undertaken to develop different techniques to improve stability and reliability. It is seen that incorporation of a mesoporous layer of alumina as scaffold could bring about an improvement in efficiency. Similarly, passivation of the perovskite surface with Lewis bases like thiophene and pyridine retards recombination losses and improves both efficiency and stability (Noel *et al.*, 2014). Polymer coating the hole and ETLs could also bring about improvement in stability (Habisreutinger *et al.*, 2014a) as well as functionalization of hole and electron transport materials with graphene.

Material Challenges

Organic-inorganic hybrid PSCs fabricated now-a-days rely primarily on organic molecules such as methylammonium, ethylammonium, or formamidinium, forming trihalide plumbate perovskite materials for high efficiency, improved charge mobility, long diffusion length, and reduced recombination losses. But the organic molecules are prone to damage by moisture, UV radiation, and temperature, thus deteriorating device performance within a short time span. There are reports of maximum stability values of just over 1000 h. It has been observed that moisture treatment of PSCs during device fabrication has a positive influence on their stability. The devices which have been exposed to moisture during fabrication have greater capacity to retain their maximum PCE for a longer time. Moreover, the materials being the cynosure of attention are plumbahalides and that Pb is a toxic element is common knowledge, so use of lead is a serious cause for concern. Hence, research is being undertaken on replacing Pb. Sn has been the most suitable candidate thus far in fabricating lead-free perovskites. Methylammonium tin iodide ($\text{CH}_3\text{NH}_3\text{SnI}_3$) perovskite, a direct-gap light absorber with an energy gap of 1.3 eV (Hao *et al.*, 2014) is an apt candidate to substitute methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) perovskite with a band gap of 1.55 eV. Mixed methylammonium halide perovskites are also being investigated, such as $\text{CH}_3\text{NH}_3\text{SnI}_{3-x}\text{Br}_x$ to cover much of the solar spectrum. The Sn (II) compound formamidinium tin iodide ($\text{NH}_2\text{CH}=\text{NH}_2\text{SnI}_3$) (Mitzi and Liang, 1997) adopts a similar cubic crystal structure as $\text{CH}_3\text{NH}_3\text{SnI}_3$ at room temperature. A solid solution with $(\text{CH}_3\text{NH}_3)_{1-x}(\text{NH}_2\text{CH}=\text{NH}_2)_x\text{SnI}_3$ is also a possibility. Tin halide perovskites open up a new avenue toward low-cost environmentally friendly solar cells. Sn is successfully being used in some solar cells but it suffers from the drawback that Sn^{2+} gets oxidized to Sn^{4+} in the atmosphere and thus loses the perovskite structure, degrading device performance. Research is in progress to look for suitable remedies for these problems. Furthermore, the organic hole transporter being most frequently used and yielding the highest PCE, spiro-OMeTAD, is not only an expensive material but also susceptible to moisture and temperature degradation. Thus the devices using spiro-OMeTAD may degrade in presence of moisture because of the organic HTM used. To overcome this problem different HTMs such as those with carbon-based materials like a double layer of P3HT/SWCNT (single-walled carbon nanotubes)-PMMA (poly-methyl methacrylate) have been investigated. They have demonstrated good thermal and moisture stability. The one with a triple layer of $\text{TiO}_2/\text{ZrO}_2/\text{C}$ as a scaffold has also been successful. The carbon layer plays an important role in water resistance.

Device Challenges

The perovskites have attracted much attention of late, one of the reasons being the ease of fabrication of these devices from inexpensive solution-processed methods. But the layers deposited from solutions sometimes lack uniformity as well as being inherently infiltrated with trap states and imperfections. These may lead to interfacial recombination and hence loss of efficiency and device stability. To overcome these problems the trapped states are often filled up with Lewis bases like thiophene and

pyridine for better pore-filling to retard charge recombination. The electrons and holes from the photoexcited perovskite once extracted through the electron and hole transporting layers should not be allowed to recombine and thus there is an optimum thickness of the different layers of the solar cell which must be maintained. But the optimum thickness is still an open question as it tends to vary from device to device based on the materials being used.

Conclusions

Thin-film photovoltaics can reduce the fabrication cost of solar cells as compared to conventional silicon solar cells. Several approaches like nanocrystalline solar cells, organic solar cells, quantum dot-sensitized solar cells (QDSSCs), DSSCs, and of late PSCs have come to the forefront of photovoltaic research. The PSCs have evolved from DSSCs and have become desirable because of their capability of broad light absorption, high open circuit voltage, ambipolar nature, and widely tunable characteristics. The organo-trihalogen plumbate perovskites are being used as the absorber, often coated upon the surface of alumina or titania to form a mesoporous PSC. Other varied architectures like planar heterojunction, hole-conductor free are also being implemented. Metal oxides such as TiO_2 and ZnO are most widely used as blocking layers because of their ability to prevent recombination and leakage currents. But the synthesis of these materials requires high temperature sintering. In order to augment the process abundant materials which can be synthesized from inexpensive solution-processed methods like carbon, graphene, GO, CNTs, and fullerenes are being incorporated into PSCs. These nanostructured materials help to increase the area of contact between interfaces, thus aiding efficient charge accumulation and separation. Nanostructured materials are highly in demand because of their excellent surface-volume ratio for efficient sunlight absorption and effective functioning of PSCs. But organic-inorganic hybrid PSCs are susceptible to moisture, UV radiation, and temperature due to the organic radicals and hence these devices are prone to degradation in ambient conditions and are therefore unreliable. Various approaches like TiO_2 scaffolding, passivation of trap states with Lewis bases like thiophene and pyridine, use of polymer coated CNTs as well as triple layers of $\text{TiO}_2/\text{ZrO}_2/\text{C}$ to retard moisture ingress have been successfully implemented to prolong the lifetime of the solar cell devices. There is also immense prospect for the fabrication of multi-junction hybrid solar cells in future. By absorbing high-energy photons in a wide band gap solar cell, allowing low-energy photons to pass through the first cell and be absorbed in a narrow band gap solar cell, would result in an efficient absorbing of the solar spectrum and reduced energy loss. An all-PSC concept is as attractive as that of a hybrid tandem device with a top perovskite cell and the bottom cell composed of crystalline silicon. This new avenue of research regarding PSCs would be a reliable source of clean energy in future only if their stability issues can be resolved. There is immense prospect for clean energy generation from these devices in future. The solar panels of tomorrow might not only be transparent, lightweight, flexible, and ultra-efficient with the usage of perovskite materials, but also it would be possible to coat them on skylights or windows. Perovskites are promising innumerable applications such as photovoltaic curtains, building-integrated photovoltaics, wearable electronics, and tandem devices (Eperon *et al.*, 2014; Li *et al.*, 2014b; Bailie *et al.*, 2014) and immense capability of overcoming the persistent energy crisis of the world and becoming the source of energy in future. Although research is still in its infancy, in the future, nanocrystal perovskite photovoltaics may offer advantages such as flexibility, lower costs, clean power generation, and better efficiency. The PSCs should meet stringent requirements in terms of PCE, cost, and stability and there is immense prospect for them to achieve these objectives.

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Nonsurfactant Sol–Gel Route Synthesis of Nanoscale Powder Production

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Introduction

Nanotechnology help human to lead a better life in the 21st century. Owing to the diverse applications of nanotechnology-led products or materials, several investigations were conducted over the years in the quest to find novel nanoporous materials with new or improved properties such as new surface structure, morphology, pore orientation, pore shape and overall architectures. In order to achieve these objectives, many studies were focused on the synthesis methodology. In a typical synthesis procedure of mesoporous silica *via* carbon-templating method, the use of designer organic molecules of surfactants were employed. These surfactants will then direct themselves to self-assemble forming micelles core that finally become the pore spaces after removal by calcination (Matsumoto *et al.*, 2004). The use of surfactants as structure directing agents in carbon-templating method to synthesize nanoporous silica materials were widely adopted method since their first discovery. By employing specially designed surfactants in carbon-templating synthesis method, several kind of morphologies of the nanostructured inorganic oxides were observed. Such morphologies include nanotubes, nanospheres, nanoplates and were achieved by manipulating the synthesis procedures and compositions.

Nonsurfactant route of sol–gel carbon-templating method have been a growing interest in the field of mesoporous materials synthesis. This approach was favored due to their versatility in the synthesis approach. Additionally, the high cost and the difficulty to dispose the synthesis by-products when using surfactant as carbon template are major problems in sol–gel synthesis method. The nonsurfactant method is expected to be cost-effective and facile synthesis approach of producing mesoporous materials in an attempt to scale-up production for industrial use. Several organic bulky molecules had been studied to substitute the surfactant carbon template to direct the synthesis of mesostructured materials. Nonsurfactant carbon- templating approach uses various small molecules that can form aggregations or pre-polymers. On these aggregations of small molecules are where the hydrolysis and condensation-polymerization of the inorganic precursors were able to take place during the synthesis. Recently, several new methodologies that are facile, innovative and cost-effective were introduced such as using organic molecules other than surfactants and modifying synthesis methods to induce porosity in the materials. It is still a great challenge to produce mesoporous materials without the aid of self-assembling surfactant micelles. Some studies had attempted to substitute the surfactants with several potential small molecules such as glucose and dye molecules. However, these approaches were restricted mainly due to the complex designer molecules that were needed during the synthesis process. Therefore there is a need to substitute the carbon template from specially designed surfactants with carbon template originating from direct decomposition of hydrocarbons derived from biomass such as palm oil, corn oil, etc., which is a greener and cost-effective synthesis approach (Misran *et al.*, 2008).

Sol–Gel Method

The most documented route for the preparation of nanoporous inorganic materials was the sol–gel route employing the use of surfactants molecules. Traditionally, sol–gel processing is widely used not only in the preparation of mesoporous silica but applied in the preparation of ceramics, thin film, coatings over porous membranes and composite materials combining benefits from glass and plastic technologies. The most useful feature of sol–gel processing is the ability of forming homogeneous and pure product at a wide range of temperature, most commonly at room temperature or below (Lesaint *et al.*, 2005). A sol is defined as a colloidal dispersion of solid particles in liquid. On the other hand, a colloid is a suspension in which the dispersed phase is small ($\sim 1\text{--}1000\text{ nm}$) that gravitational forces are negligible. These interactions were dominated by short-range force such as van der Waals attraction and surface charges (Che *et al.*, 2003; Brinker and Scherer, 1990). In sol–gel process, the preparation of colloid started with a metal or metalloid element surrounded by various ligands (appendages not including another metal or metalloid), called an alkoxide.

In general, the sol–gel process is a wet chemical method involving hydrolysis and co-condensation of metal alkoxides and inorganic salts. In this method, alkoxide molecules undergo condensation to form a siloxane (--Si--O--Si--) network. A soluble silicate such as sodium silicate or silicon alkoxide (alkoxysilanes, Si(OR)_4) with R groups being methyl (CH_3), ethyl (C_2H_5) or propyl (C_3H_7) are used as the silica source. The most studied alkoxide is tetraethylorthosilicate (tetraethoxysilane-Si (OC_2H_5) $_4$, TEOS).

In the synthesis method using alkoxy species, the hydrolysis of alkoxy groups precede the condensation with a neighboring hydroxyl groups such as silanols (Si–OH). Hydrolysis and condensation occur at the same time in aqueous alkoxide solutions. Silica sols are obtained when mixing the liquid alkoxide with water. Condensation process enables the formation of stable particles in colloidal size inside silica sols. As the condensation reaction progress, the three-dimensional siloxane networks are gradually formed. The condensation reaction is influenced by the addition of salt and the change in pH condition. Both factors will determine whether the reaction will go to the direction that will further increase the particle sizes or to the direction that will promote more siloxane linkages to form chains as shown in schematically in Fig. 3. Regardless of two different reaction paths, the viscosity of the solution will increase drastically. At this point where the elastic stress is exceeded, the silica sol will condense to a gel. The as-formed gel is called *hydrogel*. If the solvent used is alcohol, the as-formed gel is termed *alcogel*. Drying in air the as-formed gel will result in the loss or evaporation of the pore-filling liquid and the resulting gel would have reduced pores, subsequently known as *xerogel* (Vansant *et al.*, 1995). If the as-formed gel is dried under supercritical condition, the effect of capillary forces can be eliminated completely thus resulting in a gel with large pore volume (up to 98% of the total volume) which is subsequently known as *aerogel*.

Hydrolysis Process

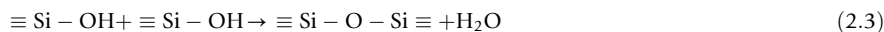
Sol-gel silica synthesis is highly depended on the controlled condensation of Si(OH)₄ species [69]. These may form from the reaction of soluble metal alkoxides or metal silicates precursors with water. The reaction is called hydrolysis. Metal alkoxides are popular precursors because they readily react with water. Hydrolysis of sodium silicate occurs at controlled pH. At pH below 7, silicic acid monomers of Si(OH)₄ exist. At higher pH, anionic silicic acid –Si(OH)₄ species are predominant. Hydrolysis reactions for alkoxide precursors as shown in Eq. (2.1) and sodium silicate precursor as shown in Eq. (2.2) shown below:



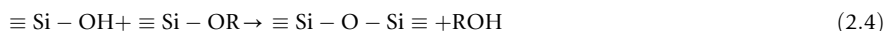
R denotes the ligands such as methoxy (OCH₃)₄, ethoxy (OC₂H₅) etc. On the other hand, alkoxy silanes are insoluble compounds in water. Thus, a homogenizing agent of short chain alcohol is needed. However, in the absence of an alcohol, the hydrolysis process will self-generate the needed alcohols as by-products. Furthermore, to escalate and complete the hydrolysis process, catalysts in the form of acids or bases are needed. In both condition, the hydrolysis occur by a nucleophilic attack of the oxygen contained in water to the silicon atom (Brinker and Scherer, 1990).

Condensation Process

The polymerization to form siloxane bond occurs by either alcohol-producing condensation or water producing condensation reaction. The silicic acid monomers Si(OH)₄ condensed with each other to form siloxane bonds by releasing water molecules.



In addition, hydrolyzed alkoxy silane with silanol group may also condense with other alkoxy silanes molecules releasing an alcohol.



Hydrolysis and condensation occur simultaneously during the sol-gel processing. Depending on the rate of hydrolysis and condensation, the sol structures is determined. Moreover, in acidic condition, hydrolysis occurs faster than condensation and as a result, the number of siloxane linkages around the silicon central atom increases, the rate of condensation becomes slower resulting in a weakly branched polymeric network (Brinker and Scherer, 1990).

On the other hand, in basic condition, condensation occurs faster than hydrolysis. The rate of condensation increases as the number of siloxane linkages increase resulting in a highly branched networks (Brinker and Scherer, 1990). Thus, larger, bulkier and ramified polymers are obtained. Due to the difference in hydrolysis and condensation rate, the gel obtained under acidic condition exhibited slit-shaped micropores with fibrous or plate-like morphology (Che *et al.*, 2003). However, for the gel prepared under basic condition, the pores obtained was cylindrical with spherical morphology (Che *et al.*, 2003). The different properties of gel prepared in different environments was determined by the polymerization and growth mechanism of the silica sols. The branching and cross-linking polymerization of Si(OH)₄ is different from organic polymers. There are three stages involving the silicic acid polymerization: (1) polymerization of monomers to form small primary particles, (2) growth of primary particles and (3) linking of particles into networks and branched chains which leads to the thickening of the liquid to form a gel. Step (2) and (3) can be controlled by controlling the pH values and whether electrolytes (salts) are added to induce flocculation as schematically shown in Fig. 1 (Che *et al.*, 2003; Brinker and Scherer, 1990).

Gelation

As the degree of polymerizations increases, the silica networks or linkages extend throughout the silica sol transforming it into gel. Gels are defined as “strong” or “weak” according to the bond connecting the solid phase that are either permanent or reversible.

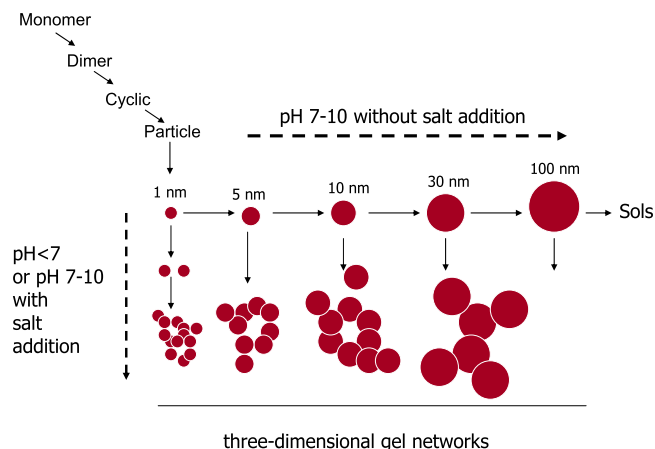


Fig. 1 Polymerization behavior of sol-gel in several environments.

This property is highly dependent on the gelling time because the sol-to-gel transition occurs gradually (Brinker and Scherer, 1990). The change is easily observed qualitatively by the color and textural change from clear to opal-like to white (Brinker and Scherer, 1990). The simplest picture of gelation is that clusters of particles grow by condensation of polymers or aggregation of particles until the cluster collides and links form between the clusters to produce a single giant clusters that is called a gel. With time, they progressively become connected and the stiffness of the gel increased. However, it is difficult to measure this transition quantitatively. The point of which gelling occurs is called gelation point, t_{gel} (Brinker and Scherer, 1990). The gelation point is not an intrinsic property of the sol but it is determined by pH value, size of container, addition or absence of salt, type of anion present, type of solvent and type of inorganic species present in the solution. The importance of gelation process is that it influences the resulting pore structure. Fast gelation will result in an open structure because the particles are cross-linked faster and cannot undergo further rearrangement. Pienaar *et al* (Pienaar *et al.*, 2007). and Liu *et al* (Liu *et al.*, 2002). studied the effect of gravity force on the gelation process. Gravity significantly influenced the gelation process by promoting intramolecular and intermolecular condensation reactions. On the other hand, acid-catalyzed silica sol polymerization under reduced gravity force exhibited preference for intramolecular condensations and densifications. This process resulted in the formation of extended coils, cycles and cages *via* cyclization reaction in sol into highly condensed gel.

Aging

The gel obtained after the transition of sol-to-gel consists of weakly formed silica networks. Aging process is done by leaving the gel in contact with the pore-filling liquid to further develop and strengthen the silica networks. The porous structure and surface area are affected by the aging treatment through four consecutive processes that occur; (1) polycondensation, (2) syneresis, (3) coarsening and (4) phase transformation (Che *et al.*, 2003; Brinker and Scherer, 1990). Polycondensation is a further condensation reaction that occurs between the hydroxyl containing species such as silanols and alkoxy groups in the gel long after t_{gel} had passed. This is to increase the connectivity of porous network. This process resulted in the strengthening and densification of the siloxane network. Syneresis is the shrinkage of the gel network resulting in the removal (expulsion) of the liquid inside the pore. The shrinkage is caused by the condensation of surface silanol groups inside the pore causing the pore to become narrower. In addition, capillary forces exerted by the pore-filling liquid on the pore wall contributed to the shrinkage. Coarsening or Ostwald ripening is the process in which the solution and redeposition of small particles driven by the difference in solubility between surfaces with different radius of curvature. Greater the curvature, higher the solubility of the smaller particles. Thus, the smaller the particle, the greater the solubility with the small particles dissolved and redeposited on larger particles. As a result, larger particles will be formed. The small cavities between the smaller particles will be filled and the neck adjoining the smaller particles will grow. This will increase the pore size but will decrease the surface area. Finally, phase transformation will occur depending on the parameters applied during the synthesis. The structural changes that occur during aging have important effect on the drying process.

Drying

In the drying process, the *alcogel* or *hydrogel* obtained are converted into *xerogel*. The gel volume that decreases is equal to volume of the liquid lost by evaporation. Shrinkage of the gel is due to capillary forces exerted by the pore-filling liquid to the pore wall. The

greatest changes in volume, weight, density and structure occur at this stage. Then, the shrinkage will cease because the dried gel network had reached some considerable stiffness. This point is marked as critical point where up to this point the pores remain full of liquid. At this point the capillary forces are at the highest value though further shrinkage does not occur. Thereafter, the liquid escapes from the pores by evaporation within the pores and by the diffusion of vapor to the surface. Consequently, the capillary forces reduce and there are no further changes to the structure of the gel network.

Nonsurfactant Sol-Gel Synthesis Method

Carbon-templating method without using surfactant use various small molecules that can cluster together and form aggregations known as pre-polymers that formed single insoluble monolayers where the hydrolysis and condensation-polymerization inorganic precursors took place similar to those on micelles formed from surfactant molecules.

What Substances Form Insoluble Monolayers?

Insoluble monolayer is unique. Only certain types of molecules are capable of forming monolayers. The stability of a foreign monolayer at a liquid-gas interface of water surfaces under normal ambient temperature and pressure or any other given condition is highly dependent on all substances involved delicately balanced. Generally, Langmuir categorized the monolayers into two. The first type consists of simple non-polymeric substances which are insoluble but whose molecules have sufficient attraction for the sub-phase (mostly water) to allow them to spread and disperse at the surface. The second type consists of a wide range of organic molecules such as proteins and synthetic polymers that are adsorbed at the liquid-gas interface. There are wide varieties of molecules that can form stable monolayers under ordinary condition, which is very beneficial in the technological and biological importance.

Insoluble Monolayers From Fatty Acids and Fatty Alcohols

Long chain fatty acids and alcohols are considered as classical molecules that can form insoluble monolayers at the air-water interface. They are classified as molecules having large non-polar (hydrophobic) portion consists of hydrocarbons and at one end polar or hydrophilic group such as $-\text{COOH}$ or $-\text{OH}$ groups. The balance between the polar and non-polar groups determines whether they will form insoluble monolayer. Short chain fatty alcohols such as methanol and ethanol as well as acids such as acetic acid are completely miscible with water. As the hydrocarbon carbon chain length in the fatty alcohols increased, water solubility decreased. For example, valeric acid ($\text{C}_4\text{H}_9\text{COOH}$) and amyl alcohol ($\text{C}_5\text{H}_{11}\text{OH}$) both dissolve at the same extent of ca. 3g/100 mL of water at room temperature (Gaines, 1966).

Straight-Chain Fatty Alcohols as Nonsurfactant Template

A greener synthesis approach can be adopted by substituting surfactants molecules with carbon template originating from direct decomposition of hydrocarbons derived from biomass such as aliphatic or fatty alcohols. Fatty alcohols are possible to self-assemble at the air/water interface to form monolayers with rich phase behavior (Gaines, 1966). Thus, fatty alcohol is suitable candidate to substitute surfactant molecules in the nonsurfactant carbon templating sol-gel method. The attempt to produce mesoporous silica without surfactant carbon templating surfactants were successful to synthesized high quality mesoporous structure [my paper].

Palm oil derived fatty alcohols bearing several carbon chain lengths (octyl, decyl, dodecyl and tetradecyl alcohols) to generate carbon template in situ for the formation of mesoporosity (Misran *et al.*, 2007a, 2007b, 2006).

Other Organic Molecules Used in Nonsurfactant Synthesis

Organic molecules that can cluster together to form insoluble monolayers by forming pre-polymers are suitable to substitute the surfactant molecules. Several small organic molecules that can cluster together into pre-polymers to form monolayer at the water-air interface similar to those formed when using surfactant molecules.

In a nonsurfactant sol-gel approach of mesoporous materials, tartaric acid was employed as carbon template or pore forming agent (PRA) together with metallic chloride as the metal precursors (Pang *et al.*, 2001). It was found that as metal loading increased, pore volume and pore diameters also increased due to presence of metal salts that promoted phase separation between silica and tartaric acid. The metal cations from metal salt precursors, such as Mg^{2+} and Al^{3+} coordinated well with tartaric acid to form carbon/metal complexes that act as pore forming agent.

Nonsurfactant carbon templating using sol-gel route using *D*-glucose molecules was also attempted. It was found that the resulting materials exhibited significant increment of pore volume and pore size as concentration of *D*-glucose molecules in sol-gel solution was increased up to 45 wt% (Wei *et al.*, 1999). At *D*-glucose concentrations of less than 36 wt%, both micropores and mesopores were present in the sample while at concentration of more than 36 wt% to 64 wt% the pore types dominant in the materials was mesopores. Hydrogen bonding between the *D*-glucose aggregations and anionic silicate species had helped directed mesophase formation. A similar observation was reported when using dibenzoyl tartaric acid (DBTA) molecules as the carbon template (Feng *et al.*, 2000). A similar attempt on nonsurfactant approach using *D*-fructose as carbon template in nonsurfactant sol-gel synthesis of phenyl-containing hybrid organic-inorganic mesoporous silica was done with additional step of pre-hydrolyzation of silica and organic precursors in acidic condition followed by the addition of *D*-fructose (Wei *et al.*, 2004). Then, the resultant homogeneous solution was dried in vacuum to obtain nanoporous powder. It was suggested that 50 wt% of *D*-fructose was optimum to produce mesoporous materials. It was suggested that the increment of surface area and pore volume increased as template molecules was increased due to increment of internal voids concentration that was previously occupied by the *D*-fructose molecules where upon extraction the space became mesoporous structure (Kaneko *et al.*, 2003). The mesoporosity in the materials prepared by this nonsurfactant route was suggested to form from the template aggregates or assembly of several aggregates and the porosity was highly dependent on the *D*-fructose contents in the starting mixture.

Mesoporous titanium dioxide based on a nonsurfactant sol-gel using urea and β -cyclodextrin(CD) as mixed carbon templates (Zheng *et al.*, 2001). However, increment or decrement of the urea and CD as carbon template played no significant role in controlling the pore sizes and pore volume as observed in other nonsurfactant carbon template systems even though the interactions between the carbon template molecules was found to increase when urea and CD was used.

In the nonsurfactant approach using silicate precursors, synthesis and drying processes were done in vacuum where the coprecipitation of sodium silicate and metal salt solution of aluminum nitrate (Yao *et al.*, 2002). Then, the silica-alumina precipitate was re-dissolved to obtain a precursor sol and aged in vacuum to obtain the transition of sol-to-gel to yield mesoporous materials containing aluminum metal.

Thermoplastic polymer such as polymethyl methacrylate (PMMA) was also used to prepare nanocomposite in the surfactantless method by forming stable colloidal dispersion of precursor sols (Percy and Armes, 2002). In this synthesis method, silica sols containing 13 nm sized silica particles achieved stable colloidal dispersion up to 58 wt% without any addition of surfactant. The obtained sols were reacted with PMMA by repeated centrifugation-redispersion technique to obtain PMMA/silica nanocomposite.

Nonsurfactant approach can be applied in the synthesis of ceramic hollow particles. Hollow monodispersed spherical silica particles were synthesized without any surfactant or template by employing a two-step acid-base catalyzed reaction of phenyltrimethoxysilane (PTMS) (Hah *et al.*, 2003). The hydrolysis of PTMS occurred in the acidic condition followed by the condensation of silane in PTMS to yield monodispersed hollow silica microspheres. It was found that the hydrolysis time was crucial in the formation of hollow spherical silica at ca. 0.4–4 min as the reaction time (Hah *et al.*, 2003). Longer hydrolysis time resulted in dense microspheres. In the formation of hollow silica particles, under stirring condition, droplets of PTMS were formed and the size gradually decreased and becomes miscible with the aqueous solution as the hydrolysis progressed. However, the non-hydrolyzed PTMS still exist in the internal core of the droplets. The methanol produced during the hydrolysis of the PTMS has an effect on the solubility of the non-hydrolyzed PTMS where it caused the release of non-hydrolyzed PTMS from the core of the PTMS droplets thus creating a hollow structure. Therefore, the hydrolysis time played a crucial role in the formation of hollow spherical silica particles.

Due to versatility and cost-effectiveness of synthesis procedure, the concept of nonsurfactant approach was further extended to the preparation procedure of several nanostructured metal oxides. The nanoscale dispersions of metal and semiconductor in silicate and other metal oxide matrixes are much needed due to their unique size dependent optical, electrical and chemical properties. One favorable metal nanoparticle is gold. Several studies were conducted in the nonsurfactant synthesis approach of gold (Au) containing mesoporous silica, Au nanowires or Au nanobelts for applications in nanodevices (Cheng *et al.*, 2003; Sun *et al.*, 2004). Mesoporous Au-silica nanocomposites with high surface area was prepared using tetraethyl orthosilicate (TEOS) with gold sol in the presence of dibenzoyl tartaric acid (DBTA) as the carbon template (Cheng *et al.*, 2003). Au nanoparticles were embedded inside the three-dimensional silica network through the sol-gel process to obtain monolithic crack-free DBTA containing gold-silica gels. After the removal of the DBTA from the gold-silica-DBTA complex, mesoporous gold-silica nanocomposites were obtained. Three-dimensionally branched Au nanocrystals were also obtained from Au salt in neutral buffer solution of pH 7.5 and at room temperature (Xie *et al.*, 2007). Buffer solution acted as reducing agent to the Au salt as well as shape directing agent.

On the other hand, metal oxides with several morphologies were also synthesized using nonsurfactant route (Liu *et al.*, 2006; He, 2005; Wang *et al.*, 2005a; Joshi *et al.*, 2005). For example, ZnO with various sizes of flower-like morphology was prepared *via* the nonsurfactant route at different pH value from Zn salt precursors. The crystal growth depended on the active site on the ZnO nuclei that varies according to pH value resulting in several sizes of flower-like ZnO crystals (Liu *et al.*, 2006). In addition, ZnO microspheres with nanostructured surfaces was also prepared using this method (He, 2005). Similarly, other ceramic oxides such

as barium tungstate (BaWO_4) with controlled morphology were also prepared by using the same concept (Wang *et al.*, 2005a). Other oxides synthesis such as lithium aluminate (LiAlO_2) microbricks and rectangular nanorods were successfully done with surfactant but with additional hydrothermal treatment from Al_2O_3 nanoparticles by varying the Li/Al molar ratio with the optimum Li/Al ratio of 3 and (Feng *et al.*, 2000) (Joshi *et al.*, 2005). Selenium (Se) nanotube was also synthesized using the nonsurfactant route employing selenium salt with glucose as the reducing agent under hydrothermal treatment for several hours (Chen and Gao, 2006). The changes in the hydrothermal treatment temperature significantly affected the sizes and morphology of the resulting nanotubes.

Several efforts in nonsurfactant synthesis had employed complex molecules in the production of mesoporous silica with built-in functional groups. Kaneko and co-workers have synthesized a layered polysiloxane with built-in functional groups of alkyl ammonium ion on the pore surface with rod-like morphology (Kaneko *et al.*, 2003, 2004). 3-aminopropyltrimethoxysilane in which the hydrolysis and condensation-polymerization were catalyzed by HCl or HNO_3 under strong acidic condition without the presence of pore directing agent to obtain mesoporous hexagonal pore structure as shown in Fig. 2.

Additionally, the ion exchange properties of the synthesized materials were investigated by exchanging the amino groups with fatty acid salts as shown in Fig. 3. The diameter of the rod-like polysiloxane increased when chloride as the counter-anion, was exchanged with more bulky anion due to the increased in diameter of the rod-like micelles that would eventually stacked together to form hexagonal structure.

The mechanism of formation is shown in Fig. 4. The synthesis approach under strong acidic condition was also experimented by Wang *et al.* in producing mesoporous silica with amino functionalized group for catalysis (Wang *et al.*, 2005b).

A unique attempt of nonsurfactant synthesis approach of mesoporous silica using complex molecules was also made (Fujimoto *et al.*, 2006). In this work, an interesting complex molecule containing a trimethoxysilane group and alkyl chain attached to it *via* a carbon-carbon triple bond ($\text{CH}_3(\text{CH}_2)_{n-3}\equiv\text{CSi}(\text{OCH}_3)_3$; $n=10,16$) as shown in Fig. 5 (Fujimoto *et al.*, 2006). The

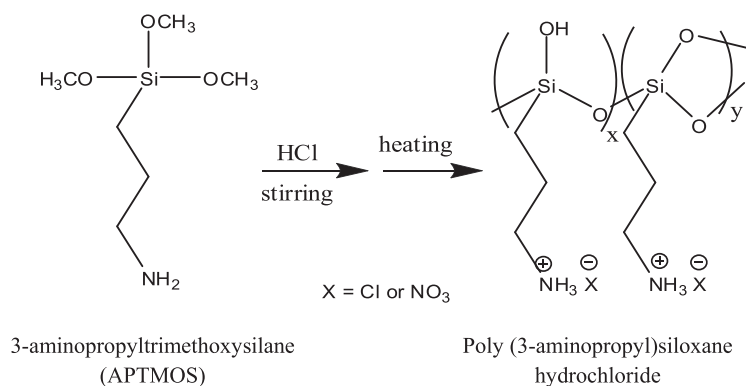


Fig. 2 Synthesis of acid catalyzed polysiloxane with ammonium functional group. Reproduced from Kaneko, Y., Iyi, N., Kurashima, K., *et al.*, 2004. Hexagonal-structured polysiloxane materials prepared by sol-gel reaction of aminoalkyltrialkoxysilane without using surfactants. *Chemistry of Materials* 16, 3417–3423.

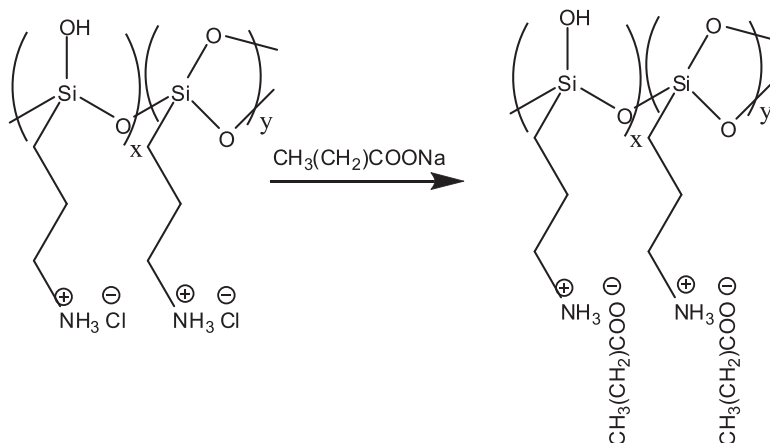


Fig. 3 Ion-exchange reaction of poly(3-aminopropyl)siloxane with sodium octanoate. Reproduced from Kaneko, Y., Iyi, N., Kurashima, K., *et al.*, 2004. Hexagonal-structured polysiloxane materials prepared by sol-gel reaction of aminoalkyltrialkoxysilane without using surfactants. *Chemistry of Materials* 16, 3417–3423.

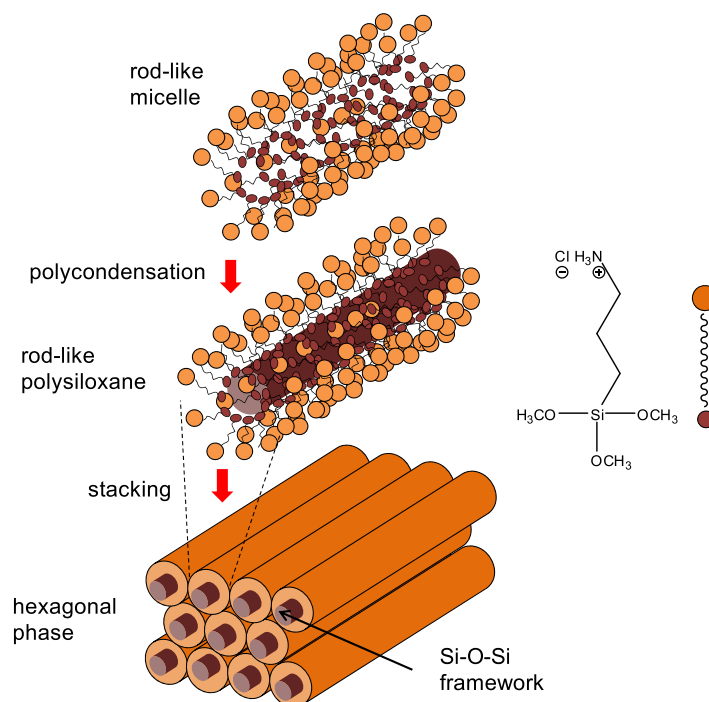


Fig. 4 Formation mechanism of rod-like polysiloxane with hexagonal phase without using surfactant. Reproduced from Kaneko, Y., Iyi, N., Kurashima, K., *et al.*, 2004. Hexagonal-structured polysiloxane materials prepared by sol-gel reaction of aminoalkyltrialkoxysilane without using surfactants. *Chemistry of Materials* 16, 3417–3423.

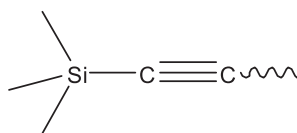


Fig. 5 The chemical structure of alkynyltrimethoxysilane. Reproduced from Fujimoto, Y., Shimojima, A., Kuroda, K., 2006. Surfactant-free synthesis of lamellar and wormhole-like silica mesostructures by using 1-alkynyltri methoxysilanes. *Journal of Materials Chemistry* 16, 986–994.

alkynyltrimethoxysilane molecules aggregates created the wormhole-like structure and upon their removal by calcination or chemical treatment with fluoride ion, yielded mesoporous materials that have wormhole-like pore structure. The pore diameter and pore wall thickness could be controlled by changing the alkyl chain length.

The non-surfactant synthesis route for producing mesoporous materials can be employed by introducing *in-situ* sugar decomposition directly onto the silica raw materials to generate the required carbon template. The silica raw material was first impregnated with sugar solution until incipient wetness was achieved followed by calcination in inert gas environment such as argon (Ar) and crystallization process (Kustova *et al.*, 2007). The resulting material, a mesoporous zeolite crystal, possessed interconnected micropores and mesoporous inside each individual crystal. Dye molecules were also possible to substitute template molecules in the nonsurfactant approach. Mesoporous silica was attempted to be synthesized using Basic Fuchsin (BF) dye as the template molecules (Xu *et al.*, 2008). Due to the planar structure of BF dye molecules, it was linked with hydrolyzed siloxane precursors to form mesopores structure with the aid of bridging molecules of aminopropyltriethoxysilane (APTES) (Xu *et al.*, 2008).

General Mechanism of Mesoporous Formation by Nonsurfactant Method

Many studies conducted on the formation of mesoporous materials without the aid of surfactant have reached the consensus with regards to the formation mechanism. In general, there are two routes for the formation of mesoporous structure. One route attempted to explain on the mesoporous formation in single crystal based on the schematic diagram shown in Fig. 6. The mechanism starts with the pre-hydrolyzed sol solution followed by the addition of liquid phase containing the carbon template to fill in the interstices between the particles. Then, the carbonization was carried out to generate the desired carbon template on the crystal. After template removal by calcination, mesoporous structure was generated within the crystal. Another mechanism pro-

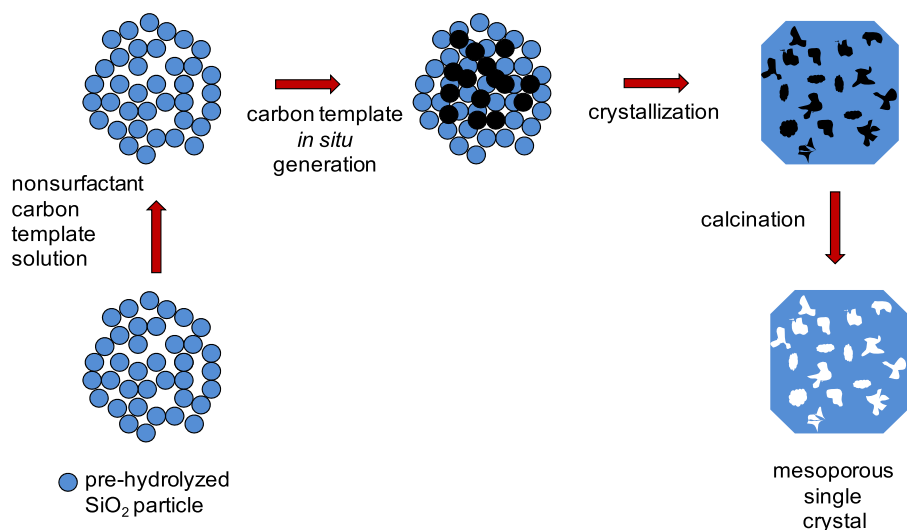


Fig. 6 Nonsurfactant templating approach to mesoporous formation in single crystal.

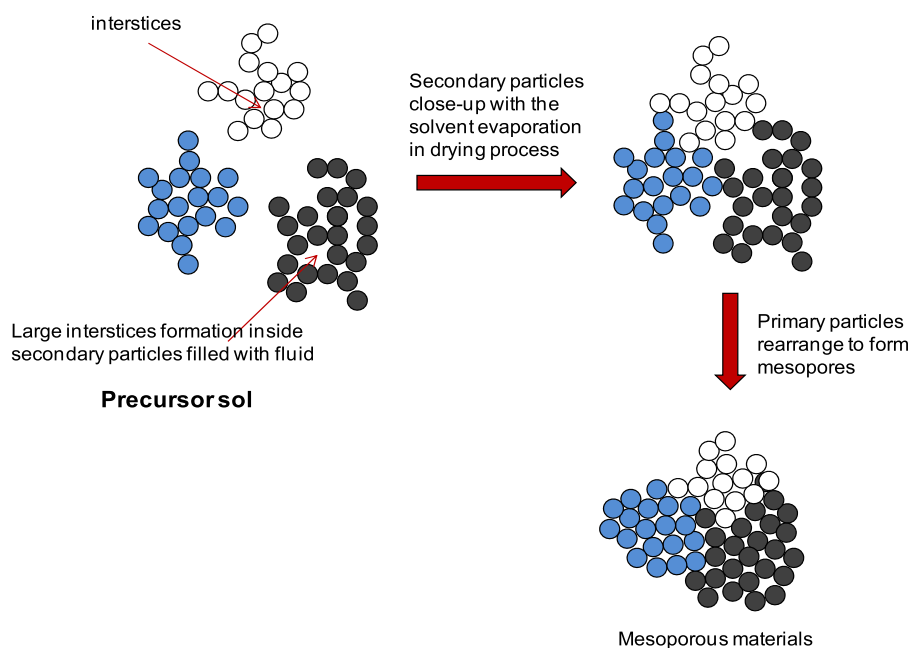


Fig. 7 Nonsurfactant templating approach to produce mesopores via interparticles aggregation (blue, gray and black particles indicates several similar aggregations).

posed that the mesopores were formed by the primary particles that had undergone rearrangements during the long drying process as shown in Fig. 7. After drying, the primary particles were closely packed together forming fluid-filled interstices that will become the precursor of the mesopores. In this mechanism, the mesopores formation solely depended only on the size of the primary particles and their arrangement during the drying process.

Conclusions

In summary, there are several possible ways to synthesize high quality mesoporous structure as well as nanosized particles by the nonsurfactant carbon templating sol-gel synthesis approach. Depending on the agents employed to form the carbon template and adopted synthesis process, the resulting materials could be tailored to suit specific applications similar to that of the synthesis procedure using surfactant. Furthermore, several bulky organic molecules have been proven to be suitable candidates to play the role of surfactants in the nonsurfactant sol-gel systems.

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Current Advancements and Future Perspectives in Electronic Materials for Developing Smart Clothing

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Abstract

Wearable technologies have created major influence on people's way of modern life by monitoring health condition. Smart clothing with the integration of wearable technology provides a sense of balance among fashion, engineering, and design and science to mitigate anticipated needs and desires by ensuring safe and secure human life. Wearable electronic materials are continuously being developed driven by the emerging innovations in sensor materials, textile materials, nanotechnology and diverse fabrication techniques. Recently, the combination of textile and wearable electronics materials and Internet-of-Things (IoT) is empowering the flawless conjunction of sensors into textiles (E-textile) leading to the development of health diagnosis and prognosis. In this paper, the current development of textile materials, sensor materials and their integration techniques to manufacture smart clothing are presented. The challenges in sensor integration and fabrication of smart clothing are also critically discussed for developing future generation smart clothing.

Key Points

- Parallel development of textile and sensor materials are continuing for new generation smart cloth.
- Provided state-of-the-art electronic materials used in developing smart cloth to support health monitoring.
- Recommended diverse integration techniques between sensor and textile materials for developing cost effective smart clothing.
- Identified current challenges of integrating sensor and textile materials.

Introduction

In the past decade, multiple features for wearable technology have been developed for monitoring human health conditions (Kosack *et al.*, 2017; Haghi *et al.*, 2017; Wang *et al.*, 2017, 2014a) by measuring heart and breath rate (Guder *et al.*, 2016; Thap *et al.*, 2016; Wang *et al.*, 2014b), wrist pulse (Nassar *et al.*, 2017), facial appearance (Su *et al.*, 2016), vocalization (Wang *et al.*, 2015; Yi *et al.*, 2015; Tao *et al.*, 2017), and metabolic rate (Imani *et al.*, 2016; Guy, 2016; Gao *et al.*, 2016; Kim *et al.*, 2018; Choi *et al.*, 2017; Liu *et al.*, 2018; Lena, 2008). However, they are required to take off, charge and put on each day, which is a burden for the users. Smart clothing concept has been advanced by integrating wearable technologies in clothes or other accessories including coat, pant, shirts, leggings, socks or shoes. Smart clothing is gradually becoming the future of wearable technologies as people feel more comfortable to use rather than a wearing an additional wristband or chest strap. Progression of Internet of things (IoT) further accelerated the development of wearable electronic materials with multifunctional and real-time sensing capabilities particularly in healthcare (Haghi *et al.*, 2017). Smart textiles act and adjust to an environment stimulus. The stimulus and the response are generated from electrical, thermal, chemical or magnetic sources. Based on operational action, smart textiles or E-textiles are classified in three types as presented in Fig. 1.

The first generation of smart textiles is a passive smart textile that contains sensors and perceived data regarding the conditions or stimuli of the environment. UV protecting clothing, plasma treated clothing, and fabric with optical sensors can be cited as examples (Vagott and Parachuru, 2018). Active smart textile is the second-generation textile that contains both actuators and sensors. The actuator works on the sensed signal either directly or from a central control unit. This smart fabric is characterized as water-resistant, chameleonic, and vapor permeable heat storage, thermo regulated, vapor absorbing, and heat evolving fabrics (Vagott and Parachuru, 2018). The third generation of textiles are ultra-smart textiles which work like a human brain due to its built-in microcomputer with the capability of cognition, reasoning and activating capacities. Spacesuits, I-wear, sport jackets, musical jackets, wearable computers are few of the examples of this type of clothing (Vagott and Parachuru, 2018).

Biocompatibility, compactness with skin, durability, size and weight are the essential features of the wearable electronic materials to ensure accurate measurement of the physiological parameters (Liu *et al.*, 2018). In addition, wearable electronic devices should have the ability of distinguishing parameters between a target and a nontarget due to the complex sensing attributes, and many diverse stimuli of the human body. Additional limitation of the wearable devices is its poor design layout and integration techniques with the human body causing discomfort while it is worn for a longer period on a regular basis. Despite the challenges, a continuous development of wearable electronic materials is taking place, motivated by the emerging innovations

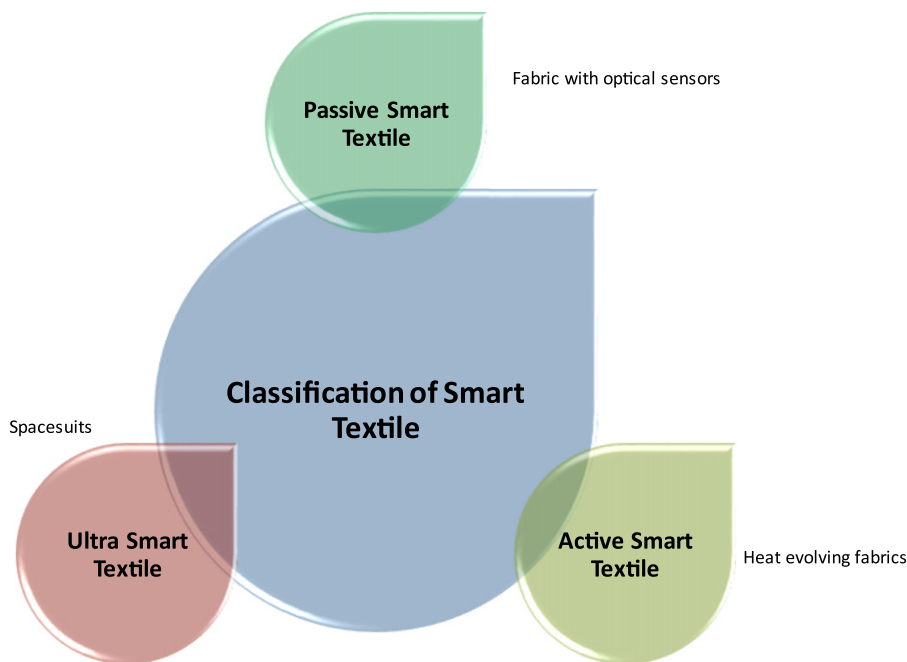


Fig. 1 Classification of smart textile. Information taken from Vagott, J., Parachuru, R., 2018. An overview of recent developments in the field of wearable smart textiles. *J. Textile Sci. Eng.* 8(4), 1-10. <https://textilelearner.blogspot.com/2013/04/an-overview-of-smart-textile.html>

in sensor materials, textile materials, nanotechnology and diverse fabrication techniques. In general, electronic material development is progressing in two directions either as a textile material or sensor material (Fig. 2).

This paper presents state-of-the-art wearable electronic materials with a particular emphasis on the smart clothing. The rest of the sections is organized as follows. Development of various textile materials for smart clothing is presented in Section “Electronic Materials for Smart Clothing” in this article. Section “Wearable Sensor Materials for Smart Clothing” has presented current development on sensor materials for smart clothing. Focus has also been given on integration between sensor and textile materials in Section “Wearable Sensor Materials for Smart Clothing”. Key challenges of the sensor integration with textile are also presented in Section “Integration Between Sensor and Textile Materials”. Finally, key conclusions are drawn in Section “Conclusions”.

Electronic Materials for Smart Clothing

The integration of textiles and sensor materials can play a great role in developing smart clothing. It is capable of enhancing traditional health monitoring system developed by rigid and non-flexible electronic products. For example, integration is accomplished by embedding the flexible devices into the textile substrate such as the electronic devices are attached into the fabric. Integration is also accomplished by attaching flexible electronic device with the fabric using glue or pressure buttons. Another example could be directly integrating electronic substrate in fabric level, yarn or fiber level and material level.

Smart Textile Layers and Components

Smart clothes present an opportunity to create an interface for the next generation of smart device between the real and digital worlds beyond the existing devices such as smart phones and portable connected devices. Fabric structures are produced using different textile fibers and processing technologies. These processes create textile design based on aesthetics and technical performances of the fabric. Firstly, fibers are processed into yarns, which are used for manufacturing fabrics by knitting, weaving, lacemaking, knotting and stitch bonding. Compound processes such as coating and lamination or coloring are also applied by dyeing or printing to enhance their functional characteristics and physical appearance. Smart fabrics can be developed at different layers by integrating sensors at the fiber or yarn level, fabric level and dyeing or printing level (Lena, 2008) as shown in Fig. 3.

Textile Materials Development

Over the past ten years, many innovative materials have been developed and used with the purpose of realizing smart clothing. Fig. 4 provides categories of selected textile materials for smart clothing.

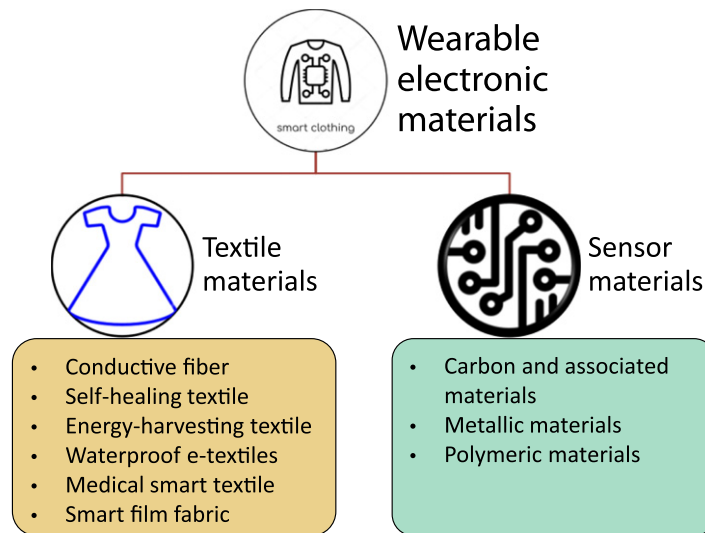


Fig. 2 Electronics material development for smart clothing.

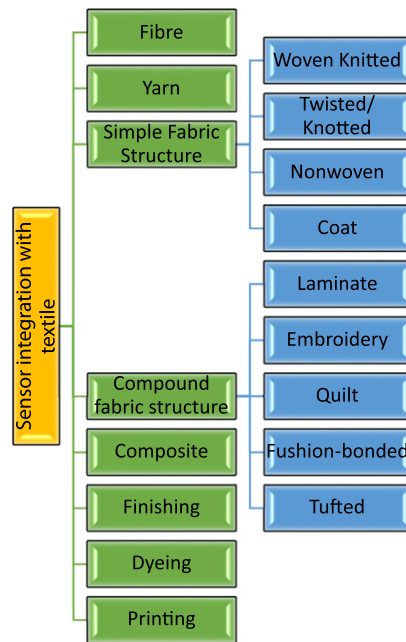


Fig. 3 Different types of textile layers for integrating sensors. Reproduced from Lena, T.H.B, 2008. Interactive Textile Structures. Department of Computer Science and Engineering, Chalmers University of Technology Göteborg, 8.

Conductive fibers

Various types of filaments are used in smart clothing as conductive fiber materials that include Copper (Cu), silver-plated copper (Cu/Ag), brass and silver-plated aluminum (Al) filaments and copper-clad aluminum (CCA) filaments (Elektrisola Feindraht, 2020). A metal forming production procedure called wire drawing is employed to manufacture the metal fiber. Drawing die is used to draw the fiber, which is consisted of a steel mount with ceramic-, carbide- or diamond-based dies. The primary diameter of the conductive wire varies based on the microstructural and mechanical characteristics of the material. For example, the primary copper wire diameter is generally 8 mm and iron wire is 5 mm. The wire is annealed at a temperature between 600°C and 900°C. Then the fine metal wire is wrapped onto a rotating wire drawing cylinder after quenching (Mac *et al.*, 2004). Some metal monofilaments are integrated with textile fibers used in weaving and knitting. At the beginning, conductive threads were utilized in many applications including military, medical and electronics manufacturing (Resistat Fiber Collection, 2020). However, electro-textiles are the textile structures that reveal conductivity (Redström *et al.*, 2005) and perform functioning in electronics, antistatic (Sophitex Ltd, 2020), electromagnetic interference shielding (EMI) (LessEMF, 2020) applications, infrared absorption or

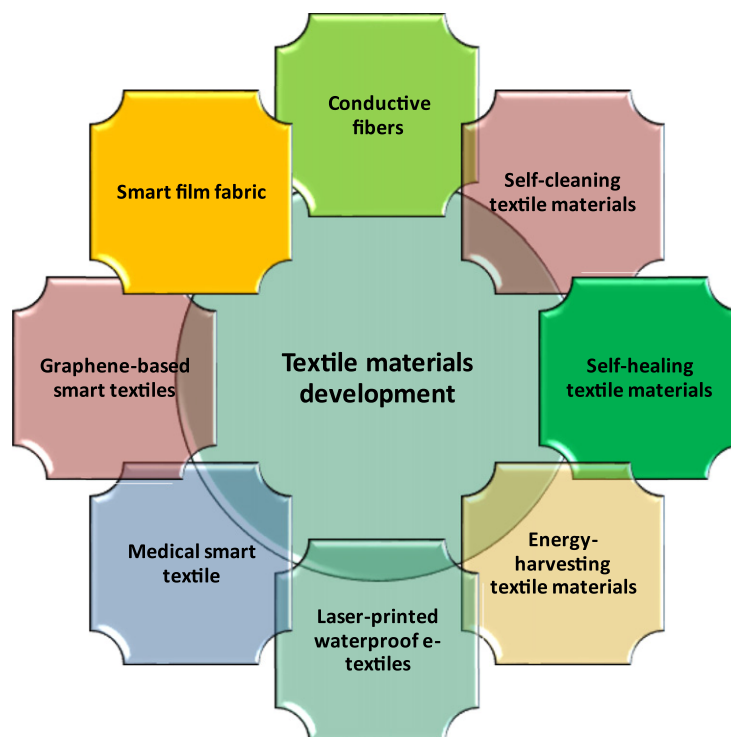


Fig. 4 Classification of textile materials for the development of smart clothing.

protection of clothes in explosive areas (McFarland *et al.*, 1999). The metal monofilaments are developed with copper, brass, bronze, silver, gold and aluminum.

Washable capability of self-cleaning clothes as futuristic fashion will attract consumers. The dirt can be broken down after exposing them in sunlight through integrating metal structures with cotton fiber. A study has been conducted for developing self-cleaning textile recently by the researchers at RMIT University in Melbourne (Self-cleaning clothing, 2019). They have integrated 3D copper and silver nanostructures woven into a cotton fabric. The ultimate target was to integrate special nanostructures into fabric that is capable of creating innovative textile for degrading dirt, dust, and sweat by the hot electrons generated from absorbing energy by the nanostructures when exposed to light. The hot electrons then break down the dirt and clean the fabric.

Self-healing textile materials

Smart clothes are usually expected to be flexible and stretchable. However, scratch and damage can potentially interrupt the device functionality and service lifetime. The embedded device in smart clothing should have the capability to maintain its basic function after mechanical damage. Self-healing is a process of maintaining the smart clothes durable by repairing any damage. Research on functionality of sensors and the capability of self-repairing is being investigated (Liao *et al.*, 2016). High signal-to-noise ratio can still be maintained by a printable paper-based strain sensor after surviving lengthwise and transacted cuts. Then the damaged sensor is placed in the operation through additional electrode adhesion and wire bonding for healing the mechanical damage. Self-healing polymers are prepared by implanting external healing agents and catalysts in capsule or vascular networks (White *et al.*, 2001). The capsule is broken by huge strains that can release healing agents into the crack region for triggering further polymerization and linking detached molecules (Dohler *et al.*, 2017). Self-healing magnetic ink is used in smart clothing components including batteries, electrochemical sensors, and circuitry.

Energy-harvesting textile materials

Clothes can be integrated with electronics such as phones for listening to music, getting directions and taking calls either by touching or pressing button or brushing a sleeve. However, it is challenging to manage charging the smart clothes on a daily basis. Furthermore, lithium rechargeable batteries have weak mechanical stability therefore, they are unable to use for powering sensors continuously (Du *et al.*, 2017). Thus, smart clothing can be used for harvesting energy generated by the human body. Energy-harvesting yarns woven into washable textiles were developed by the researchers in Georgia Tech, USA. The friction of two materials were responsible for generating static electricity. Energy was harvested from the body movement to power a sensor by stitching fabric into socks, jumpers and other clothes. Piezoelectric materials help in recovering energy from the body movement to feed Mp3 players integrated into a jacket (Seo *et al.*, 2015). A composite material was developed with the integration of piezoelectric fiber in a polymer substrate by the University of Bolton, UK to produce a structure that can offer a non-invasive power harvesting from the movement of hands or fingers (Swallow *et al.*, 2008).

Laser-printed waterproof e-textiles

In future, a new e-textile technology called laser printed waterproof smart fabrics could be popular. Low-cost rapid fabricating textile fixed with energy electronic devices have been developed by the scientists from RMIT University in Melbourne, Australia (Tao *et al.*, 2017). A waterproof smart textile patch (10 × 10 cm) has been produced within 3 min. Furthermore, it is stretchable and can be integrated with energy harvesting technologies. For example, graphene supercapacitors can be merged with solar system or another sources of power to enable laser printing into textile directly.

Medical smart textile

Human heart failure is a common chronic syndrome happened while enough blood is not passed through the heart (Liu *et al.*, 2018). Surgery and prescribed medicine are the temporary solutions for the heart treatment. Heart transplantation could be another option but most of the people cannot afford the high treatment cost. Knitted and woven fabrics used in developing a medical electronic device, which assists in monitoring the heart and vascular system to identify the development of any heart disease. A warp knitted fabric made by multifilament texture polyester fabric is used to produce the cardiac support device.

Graphene-based smart textiles

Recently, a low-cost and sustainable graphene based conductive cotton fabric has been developed for healthcare applications (Wang *et al.*, 2014b). The functionality was embedded in the cotton fabrics by reducing graphene oxide (GO) adsorbed on cotton. A group of Korean scientists has developed gas sensor which is washable and highly sensitive. Graphene coating was applied to fibers such as nylon, cotton, or polyester to check the existence of gas in the air. Graphene contains cytotoxicity to bacteria and therefore graphene coating applied on maternity clothes can prevent spreading of bacterial infections to the newborn babies.

Smart film fabric

Electronic ink and film called DuPont Intexar can transform fabric into smart clothing for monitoring and transmitting biometric signals (Liu *et al.*, 2018). For this technology, conductor made from silver works as a sensor for sensing the bio signals. Other films integrated onto textile can protect the technology from water. An app monitors the signal data. In addition, a battery-powered technology made by a resistor that releases heat. The technology helps cloths in generating heat to make the body warm during outdoor activity. The technology is also suitable for the people who are working in construction, military, forestry, mining, and infrastructure industries.

Wearable Sensor Materials for Smart Clothing

Sensing Mechanism in Smart Clothing

Current development of wearable technologies has advanced monitoring capabilities of various physiological parameters including heartbeat rate, respiration rate and temperature. Health indicators are identified as mechanical stimulations and concentrations of electrolytes or metabolites. Strain, pressure, force and vibration which are known as mechanical stimulations are transduced into electrical parameters by employing wearable electromechanical sensors through piezo resistivity, capacitance and piezoelectricity mechanisms (Jin *et al.*, 2018).

Piezoresistive sensors are flexible/stretchable electromechanical sensors that have flexible configuration, simple operation and outstanding sensitivity due to their transduction mechanism. For example, piezoresistive-based strain devices are developed with electrically conductive sensing films, which are attached with flexible substrates in order to measure temperature, pH, humidity etc (Lee *et al.*, 2016a).

High flexibility, sensitivity, robustness and stability are the key characteristics of the capacitive wearable sensors. The sensors are developed with quadripartite textile electrode and air-fluorosilicone dielectric for detecting physical parameters of human bodies. Material compressibility of the sensors can regulate the deformation resistibility for establishing a correlation with the measurement sensitivity. Sensing performance can be improved by using low modulus materials and advanced microstructures into dielectric layer (Viry *et al.*, 2014).

ZnO, GaN and PZT are commonly known as inorganic piezoelectric materials which are used for developing flexible strain/pressure sensors through coating onto flexible polymers (Liu *et al.*, 2018). However, inorganic materials are costly and therefore, piezoelectric polymer materials are useful and becoming popular in making flexible sensors. External mechanical stimuli help in generating electric charges while electromechanical interaction is occurred in few non-centrosymmetric crystal structure materials. Piezoelectric ZnO nanowires are used in nano sensors, piezotronics devices and nanogenerators due to its excellent piezoelectricity.

Recent Development of Sensor Materials for Smart Clothing

Developing wearable sensing devices having flexibility, stretchability and physical robustness are the great challenges at present. The development of new materials and fabrication strategies are crucial for attaining the compatibility of technical and operational properties (Liu *et al.*, 2018). Fig. 5 provides an overview of the sensor's material used for smart clothing.

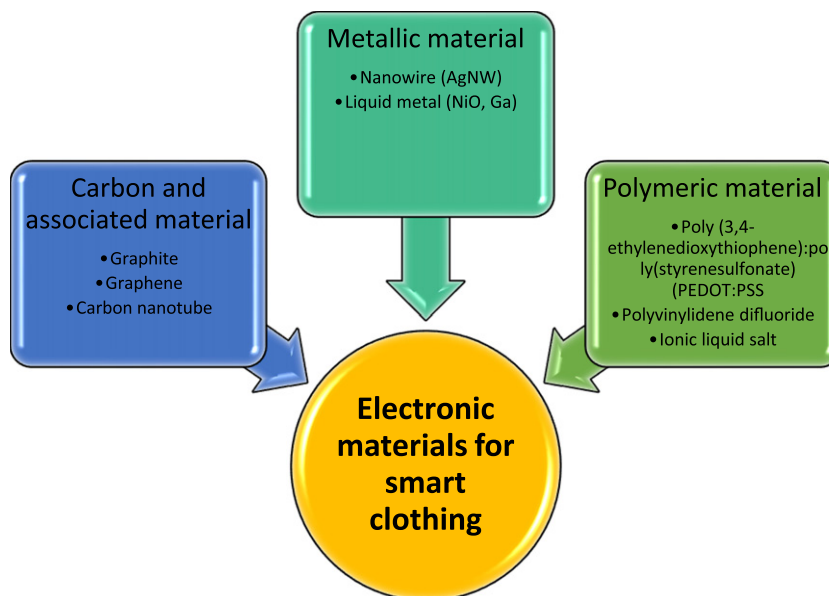


Fig. 5 Sensor materials for smart clothing.

Carbon and associated material

Graphite is developed with carbon material and used for developing pencil-on-paper electronics (Kurra and Kulkarni, 2013; Kong *et al.*, 2014). Physical frequent contact among lead tip and porous cellulose paper is responsible to rub off Graphite flakes in pencil lead during drawing process. The Graphite flakes are treated as resistor in RC filters and transistors while it is placed on paper surface. Graphene is an active material having exceptional electro conductivity, excellent mechanical properties, fantastic thermal feature and optical transmittance used for developing flexible and stretchable sensors. Laser scribed (LS) technique is useful for making graphene layer onto several adaptable substrates. Graphene woven fabric (GWF) is appropriate for wearable sensors as it contains huge micro-ribbons to adjust balance between sensitivity and stretch ability. Carbon nanotube (CNT) is one-dimensional allotrope of carbon that has electrical conductivity, highly sensitivity and strength. CNT powder is often mixed with polymer substrates and its outstanding conductivity is used for constructing sensor. To create electrodes in capacitive sensors, CNT reagent is dispersed into flexible/stretchable polymers to develop piezoresistive composites or films.

Metallic material

Piezoresistive composites and conductive ink have been developed by nanowires and nanoparticle for developing smart clothing. For building resistive-type sensors, silver nanowire (AgNWs) are embedded into Polydimethylsiloxane (PDMS). The bonding between AgNWs and polymers is lighter than carbon materials and permanent loss in AgNWs interconnection can happen at the time of loading stimuli. On the contrary, while AgNWs film is just coated on the surface of polymer where there is a great possibility to increase resistance due to buckling and wrinkling. Therefore, AgNWs layer is frequently inserted into two substrate layers. Then AgNWs are forced to push back alongside their defined paths while removing the applied load (Amjadi *et al.*, 2014, 2016). Stretchable sensors have been developed by combining with the liquid metals (e.g., mercury, gallium). Microchannel geometry is changed with the change in electric resistance through applied mechanical stimulus which is responsible in developing variations in sectional area and length of the liquid metal resistor. Thus, wearable sensing devices are developed and assembled into a RFID tag or antenna.

Polymeric material

Some organic materials can be used to develop active elements using their electro-properties. The organic sensing materials generally contain similar mechanical characteristics and have insulated substrate polymers. PEDOT: PSS known as polymer containing thermal stability, transparency and conductivity, is extensively used in sensing materials (Eom *et al.*, 2017). PEDOT: PSS has solubility in water and thus it is well-suited with dipping-drying, spinning coating and inkjet printing. However, it is difficult to apply continuous bending and stretching cycles on the dried PEDOT: PSS film as it contains intrinsic hard particles causing trigger fissure and deteriorate the film conductivity. To avoid these difficulties, PEDOT: PSS ink is frequently printed and fill into porous substrates including fabrics and cellulose paper for promoting strong bonding. Polyvinylidene fluoride (PVDF) is another energetic material used for making flexible sensors, which are used in many healthcare applications including monitoring heart rate, respiration, blood pressure etc. Wearable sensors are also built with organic materials for example PPy, P3HT and PANI (Jia *et al.*, 2014). Furthermore, ionic liquid (IL) salt helps in developing electrochemical sensors, energy devices and transistors. Strain sensors are developed by embedding IL into PDMS-based microchannel (Yoon *et al.*, 2015).

Metal filament twisted around Nylon/Lycra Yarn	• Thin conductor, elastic yarns, easy to process • Easy to break and less conductive • Non-continuous surface conductivity • Pleasant touch
Silver coated nylon	• Elastic and high conductive • Surface conductivity • Washable • Acceptable touch
Stainless steel (100%) Monofilament	• Not elastic, hard to process, high conductivity • Continuous surface conductivity • Robust and resistive to wear and tear • Unpleasant touch
Polyester (80%) Stainless steel (20%), Staple fibres	• Elastic and Low conductivity • Non continuous surface conductivity • Piezoresistive properties
Aluminium foil (100%)	• High conductive material for laminate processing • Offers a variable integration • Brittle material
Coating of Silicon/Carbon	• Semi-conductive material for coating on textile. • Piezoresistive properties

Fig. 6 Conductive materials and their properties for smart clothing. Adapted from Reproduced from Lena, T.H.B, 2008. Interactive Textile Structures. Department of Computer Science and Engineering, Chalmers University of Technology Göteborg, 8.

Integration Between Sensor and Textile Materials

Recent advances in smart sensor and textile materials can bring advantages in miniaturization and integration of smart techniques into convenient wearable or implantable devices for making smart clothing. Smart materials have several functionalities, for example, stimuli-responsiveness, capacity to generate or store charge and biocompatibility. The combination of smart materials has great potential to transform the traditional electronic systems. Fiber-based smart materials are attractive and next-generation wearable technologies are developed by incorporating sensor fibers, actuating fibers and self-powered fibers (Yongwoo *et al.*, 2019). Intelligent integration of the sensors into textiles can ensure the efficient long-lasting functionality of the smart clothing.

Conductive Materials for Integration

Yarns, coatings and films are the several forms used for lamination as conductive materials in textile. Conductivity is realised through metals or carbon where metal-based materials are mostly conductive. Various techniques are used for employing conductivity into the textile material. For example, carbon particles are melded into a coating such as silicon for developing a coating material. In addition, conductive yarns are formed using primary metal fibers, filaments of metals etc. Fig. 6 provides example of conductive materials that can be used to develop smart clothing.

Challenges of Integrating Sensors in Smart Clothing

Sensors characterized by high sensitivity, linearity, stretchability, quick response time, durability, self-power and biocompatibility are required for developing superior operation and trustworthy wearable health monitoring system. Continuing development of the sensor materials have added thrilling prospects in developing wearable sensors for future medical applications. However, systematization, intellectualization and manufacturing of wearable healthcare devices still remain some of the challenging issues. Fig. 7 presents a summary of the key challenges in integrating wearable sensors into textiles.

Most of the wearable sensors for smart clothing are not cost effective due to the inefficiency in fabrication and inconsistent in performance. Many sensor materials are manufactured by advanced processes, but it is still challenging to ensure the consistency in

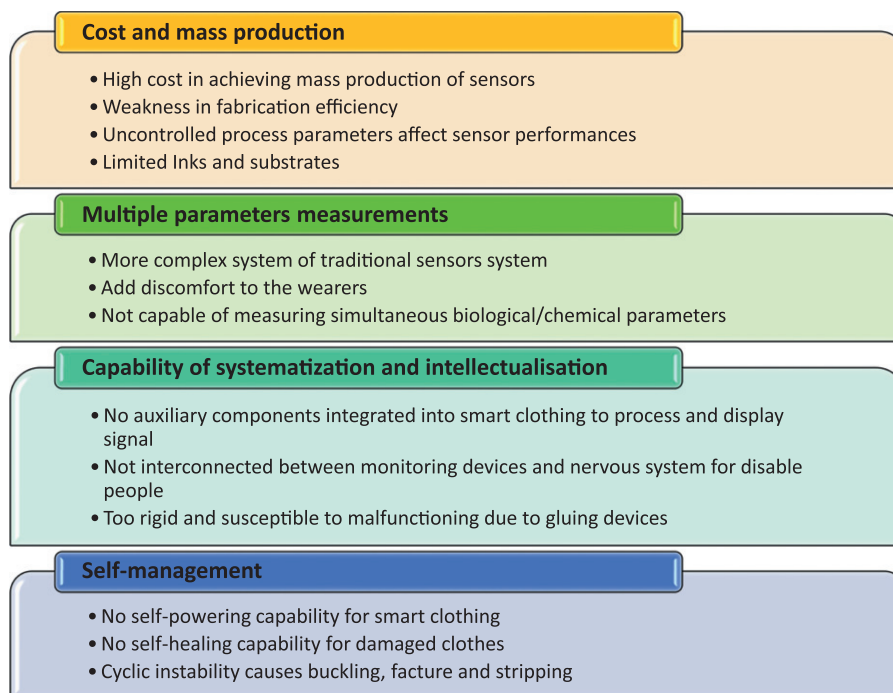


Fig. 7 Current challenges of integrating sensor and textile materials in smart clothing.

quality and to reduce the cost or processing. The usage of organic materials encourages cheap budget choices that can reduce economic burden (Liu *et al.*, 2018).

Multi-functionalization can be brought in by combining multiple sensing components into one individual pixel rather than increasing number of sensors integration with smart clothing. Proper pixel arrangement and transduction principle can be used to reduce crosstalk between these units. It is also highly challenging to measure the mechanical and biological/chemical parameters simultaneously. Multidisciplinary collaboration from engineering and material technology experts would be helpful to mitigate such problem (Liu *et al.*, 2018).

Good systematization and intellectualization can promote wearable systems globally. Systemization can be developed by inter-connecting monitoring devices and nervous system that provide neural-integrated response system for the people with having disability to restore the feeling of touch and muscle movement (Yang *et al.*, 2017). For intellectualization, the wearable system can be combined with computer or smartphone. Appropriate applications can be embedded in smartphone to obtain enough health-related information. Redesigning processing and displaying modules can mitigate the barriers on flexibility, miniaturization and incorporation of intelligent system in smart clothing. Further development on module prototype including flexible screen and thin film transistor can help in solving such integration and miniaturization issues (Lee *et al.*, 2016b; Someya *et al.*, 2005; Reeder *et al.*, 2014).

Cyclic instability is developed while the sensitive films coated on substrate are subjected to buckling, fracture and even stripping after completing numerous cycles. Besides, scratch and damage can weaken the device functionality and maintenance lifetime. Self-healing material characteristics can promote functional durability of the wearable sensors (Liao *et al.*, 2016). Furthermore, self-powering capacity without having external power supply is required for developing sustainable wearable devices. Furthermore, gluing devices to fabrics can make the system vulnerable to malfunctioning. Intelligent integration of sensor device at the fiber level would provide feasible solution to avoid malfunctioning.

Conclusions

The advancement in electronic materials for both the textile and sensors have contributed to the progress in smart clothing for monitoring health condition (Ahsan *et al.*, 2022). The development of self-cleaning, self-healing and energy-harvesting textile materials will pave the way for the new generation smart clothing. Different types of sensors based on piezo resistivity, capacitance and piezoelectricity can be integrated for detecting motion and measuring temperature, pH, and humidity. Current development of sensors materials for smart clothing are categorised based on carbon, metal and polymer. It is found that graphene-based sensor materials are becoming popular for smart clothing. Although sensors can be integrated at fiber, yarn or fabric levels, still several challenges have to overcome including high cost, optimization for mass production, measuring multiple parameters, increased system capability and self-management of sensors system. With the development of sensors material and fabrication techniques, in near future the smart clothing will enter into a new era not only for monitoring health condition but also other applications in a cost-effective and flexible manner.

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Conflicts of Interest

The authors declare no conflict of interest.

Author Contributions

All authors have equal contribution to prepare and finalize the manuscript.

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Materials for Developing Future Flexible Electronic Device

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Abstract

Achieving mobility, flexibility, biocompatibility, and functional security while lowering the expense and environmental effects are the main objectives for the next generation of wearable electronics. Flexible electronics (FE) is a promising concept which makes it possible to incorporate many technologies into daily life and promote the development of ground-breaking applications. For physically FE, mechanical properties like the bending radius and the overall thickness are crucial. This study's fundamental goal is to provide a thorough summary of the development, advancement, and applications of FE in diverse fields. The article begins by listing the flexible materials employed during the last few decades in a chronological order. The distinct structural design of flexural electronics is briefly introduced and the processing techniques for producing FE are taken into consideration. The recent developments in flexible electronic are then discussed in relation to the development of materials, such as inorganic and organic substances. The application of materials in the field of flexible electronic is finally discussed, along with potential challenges and future prospects.

Key Points

- Presented fundamental background of the conducting polymers used in wearable technology.
- Provided state-of-the-art conducting polymer as textile sensing material to support developing smart wearable.
- Provided state-of-the-art applications of conducting polymers.
- Identified current challenges of conductive polymers and integrating with textile materials.

Introduction

Modern FE has seen explosive expansion in the recent years, forcing traditional solid, long-lasting, single-shape, planar and rigid electronic gadgets to change into portable, high-performance, soft, thin, light, comfortable devices with an increasing number of add-on functionalities (Shi *et al.*, 2019). The problem with conventional electronics directly leads to the enhancement of FE technology. FE as a concept have been around for many years and recently, there has been a remarkable attention in developing FE. It is an area of research, development, pilot production, and field testing that is still quite open and developing quickly (Wang *et al.*, 2022; Shrivastava *et al.*, 2020) and it utilizes functional and structural designs of material to provide distinctive research opportunities (Chen *et al.*, 2021). Theoretically, anything long or thin can become flexible. Flexible can refer to a wide range of properties, including bendability, conformability, elasticity, lightness, non-breakability, roll-to-roll manufacturability, or vast area and these properties are prerequisites for FE. So as to maintain the high performance of the devices, FE must be able to withstand significant mechanical deformation, like stretching, bending, folding, and twisting (Wang *et al.*, 2021). Therefore, the materials used in FE must possess outstanding chemical and physical properties in addition to great flexibility in order to fulfill these ideal properties. FE are highly suited for an extensive range of fascinating new applications in many sectors for instance, flexible display and lighting technologies for textiles, home electronics, industries, and architecture, flexible screens, wearable technology with sensors which aids to monitor our routines and health, artificial skins, implantable electronics devices for better-quality medical diagnostics and imaging, and expanding the services of unmanned aircraft and robots through conformable and light-weight energy sensing and extracting devices, medical-healthcare systems, individualized mobile devices, and human-machine interface elements due to their rapid evolution (Gupta *et al.*, 2018; Baran *et al.*, 2020; Zhao *et al.*, 2021a; Trung and Lee, 2016).

The 20th century witnessed the development of FE appliances. For extra-terrestrial satellites application single-crystalline silicon (Si) solar cells (SCs) were thinned 50 years ago to increase their weight/power ratio, thus permitting a specific level of warping. These materials could be bent, wouldn't shatter, and could be molded to fit. The first FE devices or cells were made possible by this concept in the 1960s (Crabb and Treble, 1967). Single-crystal Si-wafer cells were thinned to a thickness of 100 μm to create the first flexible SC arrays, which were subsequently assembled on a flexible plastic substrate (Crabb and Treble, 1967; Ray, 1967). Brody and others invented the first flexible Thin-Film Transistor (TFT) in 1968 when they developed a tellurium-based TFT on a strip of paper and suggested employing TFT matrices for display addressing. Brody's team produced TFTs on a variety of flexible substrates during the subsequent years, such as polyethylene, Mylar, and anodized aluminum wrapping foil (Brody, 1984). Researchers obtained the maximum curvature of FE circuits in the middle of the 1980s. The first reports of hydrogenated amorphous-Si (a-Si:H) produced by a glow discharge appeared in the late 1960s, and Snell and colleagues developed the first a-Si:H TFT in 1981 for liquid crystal display (LCD) application (Snell *et al.*, 1981).

Table 1 Consecutive development trends of FE

Year	Field of application	Researcher/organization
1967	First flexible solar array	R. L. Crabb and F. C. Treble (Crabb and Treble, 1967)
1968	First flexible TFT	Brody and others (Brody, 1984)
1977	Development of conductive polymer	Hideki Shirakawa and others (Shirakawa <i>et al.</i> , 1977)
1981	First flexible a-Si devices	Snell and others (Snell <i>et al.</i> , 1981)
1983	First flexible a-Si:H solar cell	Hiroshi Okaniwa and others (Okaniwa <i>et al.</i> , 1983)
1985	Flexible e-skin sensor	General Electric (Hammock <i>et al.</i> , 2013)
1987	Development of CdS solar cell on flexible substrate	P. K. Nair and M. T. S. Nair (Nair and Nair, 1987)
1990	Flexible organic TFT	Francis Garnier and others (Garnier <i>et al.</i> , 1990)
1990	Ultralight Flexible a-Si solar cell on a transparent plastic substrate	Kishi and co-workers (Kishi <i>et al.</i> , 1991)
1992	Flexible LED using conducting polymers	G. Gustafsson and others (Gustafsson <i>et al.</i> , 1992)
2004	Flexible single crystal Si-based TFT	E. Menard (Menard <i>et al.</i> , 2004)
2009	Flexible organic LED display utilizing printable elastic conductors	Tsuyoshi Sekitani (Sekitani <i>et al.</i> , 2009)
2010	Microscale integration of parallel flexible nanowire arrays for artificial electronic skin	Kuniharu Takei (Takei <i>et al.</i> , 2010)
2013	Ultrathin flexible device	E. Menard (Kaltenbrunner <i>et al.</i> , 2013)
2013	First flexible organic LED TV	SamsungPierce (2013)
2015	A printed organic TFT with high level of electrical performance and uniformity	Kenjiro Fukuda (Fukuda <i>et al.</i> , 2015)
2016	Ultra-flexible organic photonic skin	Tomoyuki Yokota (Fukuda <i>et al.</i> , 2015)
2016-present	Flexible antennas, flexible energy harvesters, flexible health monitoring devices etc.	(Van Den Brand <i>et al.</i> , 2015; Zheng <i>et al.</i> , 2020)

Organic materials are fundamentally more flexible mechanically than the inorganic films, hence from the 1990s to the early 2000s, flexible transistors and light emitting diodes (LEDs) were developed primarily on flexible substrates using the organic materials (Garnier *et al.*, 1990; Gustafsson *et al.*, 1992; Menard *et al.*, 2004; Sekitani *et al.*, 2009). There has been a growth in the FE technology during the past twelve years. Flexible electronic devices, including energy harvesting circuits, smart sensors, radio frequency identifiers, reconfigurable antennas, smartwatches, smart clothing, hearables, skin patches and this technology brought about a significant transformation in the healthcare, medical, industrial, and entertainment sectors recently (Hayward, 2022). Table 1 illustrates the development trends of FE in various field. There is currently a lot of interest in new constituents and fabrication approaches that permit the direct manufacturing of scalable and high-performance electronic appliances on the flexible substrates. This focus now encompasses features like stretch ability and heal ability as well, which can be obtained by employing elastomeric substrates with potent molecular interactions (Kang *et al.*, 2018).

FE can be formulated from a diversity of substances, including graphene, carbon nanotubes, liquid metals, and conductive polymers (Rim *et al.*, 2016). Designing certain flexible structures has major significance for FE devices, in addition to developing novel materials to make those. This article primarily focuses on the distinctive flexible structures and materials such as organic and inorganic used to fabricate the FE, which have many uses in a variety of industries. The remainder of the paper is structured as follows: Section "Introduction" presents the structure of FE utilized in various fields. Different types of materials employed to fabricate FE devices are explained in Section "Structural Design of Flexural Electronics" Section "Flexible Electronics Materials" demonstrates the applications of FE with possible challenges. Section "Example applications and challenges" presents the outlook for the future and summarizes the current status of the FE materials.

Structural Design of Flexural Electronics

Recently, one of the research interests has been on producing stretchable and flexible devices. The invention of mechanical design, material synthesis, and fabrication techniques using soft substrates are the three main themes in flexible and stretchable electronics that are now under development. While flexible materials like plastic, polymers, conductive foils, laminates, and fabrics are used to create flexible electronic devices, their systems, can be divided into four primary functional parts: front panel, substrate, backplane, and encapsulation (Khan *et al.*, 2021; Belgacem *et al.*, 2021; Wang *et al.*, 2021b) as shown in Fig. 1. An adhesive layer is used to join all four components therefore, it needs to be suitably durable, adaptable, and chemically stable. The manufacturing process must considered when selecting an adhesive (Kaltenbrunner *et al.*, 2013). The usual operation of the flexible device would be in conflict without some degree of bending capability in all of the components (Khan *et al.*, 2021).

The rapidly expanding field of flexible multifunctional electronics serves as a constant source of design inspiration for structural, functional, and material advancements. Device's flexibility and stretch-ability are significantly influenced by its configurational design. Designs from one-dimensional (1D) to three-dimensional (3D) configurations have been designed to satisfy the aesthetic requirements and various specific applications (Tong *et al.*, 2021).

Planar-Type Structure

The fabrication of Planar-Shaped Solar Cells (PSSCs) takes place directly on a textile substrate. By using direct construction on a ready textile substrate, the PSSCs can be processed more easily than the fiber-shaped solar cells (FSSCs). These flexible SCs offer a diverse

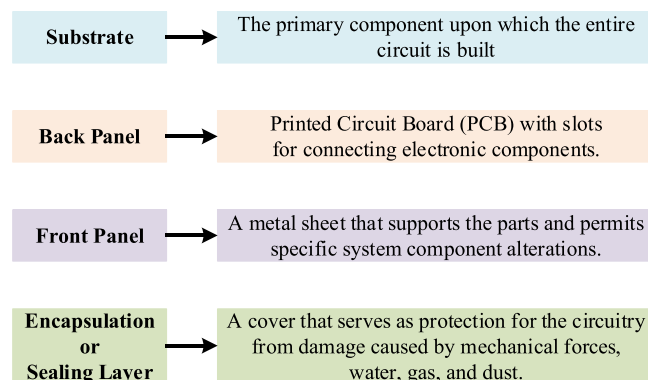


Fig. 1 Basic structure of a FE device.

range of possible applications in autonomous and battery-free electronics, which will have an influence on many industries (Hatamvand *et al.*, 2020). Because of their notable optoelectronic performance, planar organic-inorganic hybrid perovskite SCs have achieved amazing success in recent years. As a hole transport substance for planar perovskite SCs, CuO nanoparticles (NPs) are synthesized in Arjun *et al.* (2022) using precipitation, microwave, and hydrothermal assistance methods. In order to lower the defect state density of perovskite and enable effective charge transfer from perovskite to carbon, an all-room-temperature processing high-efficiency planar Carbon-based perovskite SC was developed in Deng *et al.*, 2021 that makes use of SnO₂ as the electron transport layer and a cheap polymer called polyethylene glycol (PEG) as the interface passivation layer. The grain boundary modifier of organic-inorganic hybrid perovskite films was proposed in Yang *et al.*, 2021 with a multi-functional double perovskite substance. Addition of this material provides several advantages such as promoting the progress of perovskite crystals, suppressing recombination at grain boundaries, and increasing the effectiveness of carrier collection and resulting an efficiency of 23.56%.

Electronics have urgently needed to improve their performance, adaptability, safety, downsizing, and integration of micro-batteries due to the constant development and modularization of electronics. A prototype for all-solid-state planar lithium-ion micro-batteries with great bipolar cell integration, superior volumetric energy density, exceptional flexibility, and exceptional high-temperature performance was proposed in Zheng *et al.* (2018). The layer-by-layer assembly of the planar Zn-Air battery configuration in either parallel or series makes it possible to power flexible devices with a range of voltage or current demands (Zhang *et al.*, 2021). Due to micro-supercapacitors (MSCs) excellent benefits in integration, downsizing, and flexibility, planar-shaped are preferred in FE as energy storage (ES) elements. High-performance flexible planar-type MSCs based on pseudocapacitive MoS₂ nanoparticles adorned highly conductive electrochemically exfoliated graphene (MoS₂/EEG) hybrid electrodes are inventively created in Yang *et al.* (2022a) using a straightforward and effective screen printing approach.

Fiber-Type Structure

Researchers are generating stretchable, FE with fiber-like architectures, including energy-harvesting, energy storage appliances and light-emitting components. Contrary to conventional ones, FSSCs employ flexible photoelectrodes made of inexpensive optical fibers, metal wire, carbon, etc., substantially increasing their flexibility and lowering their cost while also clearly enhancing their numerous features. The active layers are manufactured onto the cylindrical substrates of the FEECs. The non-flat shape of fiber substrates boosted the absorption of reflected and scattered light while also considerably enhancing the ability of solar cells to adapt to their environment (Hatamvand *et al.*, 2020; Kishi, 1991). The PV active layers should be coated on a cylindrical substrate (such as carbon or metal wire, thread, optical fiber, amid others) to manufacture a FSSC. In order to work, they either absorb light from the external coated layer or, in the case of an optical fiber, in-couple light from the fiber's cross section into internal PV active layers (Liu *et al.*, 2018; Zou *et al.*, 2010). With hierarchical anatase TiO₂ structures, a novel transparent, flexible fiber-type dye-sensitized solar cell (FF-DSSC), and 3D light-collected was created in Liang *et al.* (2014) (shown in Fig. 2(a)). When the TiCl₄-treated TiO₂ nanorod array is treated in a mixed solution of (NH₄)₂TiF₆ and H₃BO₃ three times, the conversion efficiency of the FF-DSSC based on the TiO₂ nanorod array increases to 4.4%, which is about four times higher than that based on a TiO₂ nanorod array treated with HCl. Another new FF-DSSCs was created in Liang *et al.* (2015) (shown in Fig. 2(b)) with 6.6% efficiency, and they have multi-working (MW) electrodes. All the parts are put together into a flexible plastic capillary tube for each MWFF-DSSC. The only counter electrode is a Pt microwire running parallel to the tube's axis, and the working electrodes are all Ti microwires that are encircled by highly ordered titanium dioxide (TiO₂) nanotube arrays.

Due to the high-performance, excellent flexibility, one-dimensional structure, and high energy density, flexible fiber-shaped energy storage (FSSES) devices are one of the promising applications of the next generation FE (Li *et al.*, 2021; Ye *et al.*, 2020). A proof-of-concept test to develop FS dual-ion batteries with good reversibility, high-energy density, and high-cycle stability was reported in Song *et al.* (2019). These devices have graphite on an omnidirectional porous Al wire for the cathode and an omnidirectional porous Al wire for the anode. Based on the combined mass of the two electrodes, the completed battery exhibits a high mass specific energy density of 173.33 Wh kg⁻¹ and outstanding flexibility in a variety of bending states. To create a flexible FS electrode with exceptional sodium storage capabilities and a novel approach for fabricating electrodes for FSSES, a one-of-a-kind

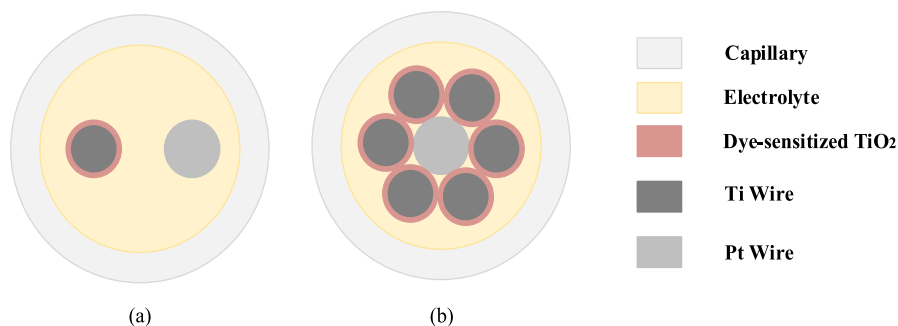


Fig. 2 Cross-sectional structure of FF-DSSC. (a) With single-working electrode. (b) With MW (six) electrodes. Reproduced from (a) Liang, J., Zhang, G., Yin, J., Yang, Y., 2014. Transparent, 3-dimensional light-collected, and flexible fiber-type dye-sensitized solar cells based on highly ordered hierarchical anatase TiO₂ nanorod arrays. *J. Power Sources* 272, 719–729. doi: 10.1016/J.JPOWSOUR.2014.09.002. (b) Liang, J., Zhang, G., Sun, W., Dong, P., 2015. High efficiency flexible fiber-type dye-sensitized solar cells with multi-working electrodes. *Nano Energy* 12, 501–509. doi: 10.1016/J.NANOEN.2015.01.023.

self-supporting nanotube array of sulfur-doped TiO₂ (SATiO₂) was suggested in [Liu et al. \(2019\)](#). It is vital to note that this battery in the form of a fiber maintained a high-reversible capacity under various bending states. Using a low-cost, effective, and scalable continuous wet-spinning approach, a flexible FS Zn-MnO₂ battery with outstanding electrochemical performance was projected in [Gao et al. \(2022\)](#). The most promising ES technology for the next portable and FE is FS supercapacitors (SCs), which can work as distinct fibers or joined fabrics and have great electrochemical characteristics and flexibility ([Meng et al., 2017](#)). The flexible FS supercapacitors are formed in [Zhang et al. \(2019\)](#) depending on the incredible mechanical characteristics of accumulated self-twisted graphene fibers. The FS supercapacitor exhibits exceptional flexibility, long-term cycling stability, high energy density, the capacitance is remarkably stable even in the knotted form. For the first time, a high-performance FSSC was built on a unique, hierarchically interconnected hybrid fiber made by in situ chemical polymerization ([Teng et al., 2020](#)).

A brand-new class of all-textile energy harvesters (triboelectric nanogenerators (TENGs)) that can directly harvest and transform mechanical energy into electricity thanks to the structural integrity of three-dimensional fabrics was suggested in [Gong et al. \(2019\)](#). Under various base acceleration circumstances, performance of a single-crystal macro-fiber composite-based piezoelectric energy harvesters was examined in [Peddigari et al. \(2022\)](#) by altering the temperatures from 20° to 70°C and the relative humidity from 10% to 90%. In a biocompatible TE fibrous films were arranged through an electrospinning method and the arranged fibrous tribofilms were utilized to manufacture a TE energy sensor and harvester ([Graham et al., 2022](#)).

Flexible Electronics Materials

In the previous two decades, the electronics sector, which mostly relies on semiconducting, conductive, and dielectric substances with micro- and nanoengineering methods, has made some exciting advancements ([Carey et al., 2017](#)). So as to withstand numerous mechanical strain/stress situations and maintain or even expand their performances, FE devices should be built using novel structural patterns for these operating materials ([Chen et al., 2019](#)). FE devices integrate both inorganic and organic substances for device fabrication with good flexibility, ductility, and processing ease ([He et al., 2019](#)). In order to attain mechanically compliant qualities, the adoption of resources are vital for FE gadgets. The performance and sustainability of devices are enhanced by appropriate materials, which expands the applications for them. [Fig. 3](#) illustrates the essential features associated with FE materials. This section will highlight the available materials and recent developments in materials used to create FE with distinctive shapes and novel functionality.

Organic Materials

In order to meet the steadily rising demand for large-area electronics, organic semiconductors (OSCs) such as small molecules or polymers are adaptable to low-cost, high-throughput manufacture due to their main characteristics of low cost and low-temperature processability over a variety of substrates ([Li et al., 2018](#)). This type of technology uses carbon-based materials, which are identical to the molecules found in living organisms ([Zhou et al., 2014](#)). Additionally, certain OSCs with advantageous biocompatibility or biodegradability properties enable organic flexible electronic arrays to easily interface with biological systems, giving rise to a variety of applications that are beneficial to people, including wearable human activity/health monitoring devices, smart prosthetics, and electronic skins. Particularly, the exceptional compliance and durability of organic semiconducting materials have been acknowledged as their considerable advantages, enabling their usage in FE ([Kim et al., 2021](#)). The advancement of organic TFT (OTFT) based electronic devices depends critically on the creation of tiny molecules and polymeric materials with great performance ([Guo et al., 2010](#)). The scientific developments in the fields of organic PVs and organic thermoelectric substances and devices were thoroughly reviewed in [Sharma et al. \(2022\)](#), with an prominence on both the creation of flexible devices and the fundamental processes. The

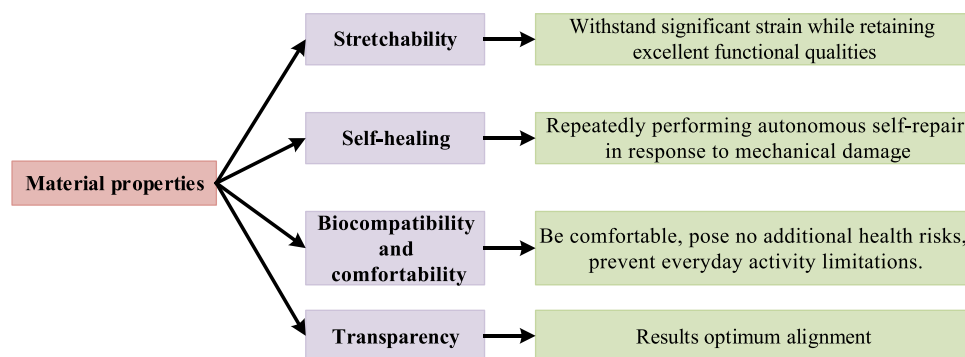


Fig. 3 Required properties of flexible electronic materials. Reproduced from Ma, Z., *et al.*, 2019. Advanced electronic skin devices for healthcare applications. *J. Mater. Chem. B* 7, no. 2, 173–197. doi:10.1039/C8TB02862A.

OSCs have PCEs of over 18%, which are equivalent to those of other SC types (Liu *et al.*, 2021). For both vastly effective solution-processed flexible and rigid planar heterojunction perovskite SCs and flexible and rigid bulk heterojunction organic SCs, a new organic small molecular hole transporting material has been rationally designed and synthesized in Reddy *et al.*, (2017). Due to OSCs distinctive advantages, such as reduced costs, lighter weight, material abundance, easy solution processing, inherently low thermal conductivity, and intrinsically high flexibility, organic materials have received lots of awareness in the arena of flexible thermoelectric generators (Masoumi *et al.*, 2022). From organic-only semiconductor devices, based on thin films of organic materials (small molecules and polymers), flexible organic electronics have advanced to nanocomposite and hybrid substances, a category of actually progressive materials formulated at the nanoscale that affords improvements in appliance performance (Silva *et al.*, 2015).

Inorganic Materials

A typical 2D substance with exceptional electrical, chemical, and mechanical characteristics is graphene. These exceptional qualities have made graphene a rapidly rising star in current years in the arena of material science and also make it appealing for utilization in FE (Yu *et al.*, 2017). Due to its exceptional qualities, graphene-based materials have demonstrated good use in a number of biosensing. A thorough analysis of the construction, synthesis, characteristics, and use of graphene and graphene-based 2D nano-materials, with a focus on biosensors and bioelectronics, has been conducted in Deepa *et al.* (2022). The best electrode materials for micro-supercapacitors (MSCs) have been thought to be 2D materials based on graphene (Yang *et al.*, 2022b). Pt and ZnO nanoparticles (NPs) on porous reduced graphene oxides were utilized to demonstrate a heterogeneous sensitization (flexible NO₂ sensors) of nanocatalysts (Kang *et al.*, 2021). Inorganic semiconductor materials, such as ZnO and ZnS, have outstanding piezoelectric characteristics and offer an extensive range of potential relevance in the domain of FE sensors (Zhao *et al.*, 2004). A full-inorganic single-junction Sb₂(S, Se)₃ SC was suggested in Salem *et al.* (2022) to increase the PCE. Other nanoparticles, in addition to 2D materials, are crucial in the domain of FE. Nanotubes, nanowires, and nanoribbons are examples of one-dimensional (1D) materials. They differ greatly from bulk materials in terms of their electrical, thermal, and mechanical properties. Since diverse 1D materials have unique electric and mechanical characteristics that make them ideal for various applications, they play important roles in the FE industry (Lou and Shen, 2016). Due to high mechanical flexibility, conductivity, and inherent carrier mobility, carbon nanotubes (CNTs) are a promising resource for inorganic FE. They can be used as the channel substances in field-effect transistors and can also be produced as films for transparent electrodes (Belin and Epron, 2005). A simple method of directly growing N, Co dual-doped carbon nanotube on carbon cloth substrate to construct a flexible trifunctional electrode was projected in Jin *et al.* (2021). An integrated power-to-gas system, a water splitting apparatus, extremely bendable zinc-air batteries, and the requisite stability may all be achieved with the electrode that was produced.

Example Applications and Challenges

Applications

FE devices have drawn numerous considerations recently owing to the potential applications they could have in the lives of today's people. As a result, FE are a key sector in the fabrication of various flexible appliances. On account of the achievement of flexible conductors, various flexible electronic gadgets such as flexible heaters, flexible storage and energy conversion appliances, flexible sensors, transistors, and artificial e-skin are manufactured with the aid of numerous manufacturing approaches (Wu, 2019). Next-generation wearable electronic applications are made possible by flexible, soft, and stretchable forms of electronics, opening up a variety of applications for healthcare, military, communication and energy uses (Vu *et al.*, 2022) shown in Fig. 4. Changing the traditional rigid, flat gadget into a stretchable electronics appliance that can conform to the curve of the human-body is an intriguing strategy for improving wear-ability in the field of human healthcare (Van Den Brand *et al.*, 2015). Because of the stretchability, transparency, and biocompatibility, FE offer a wide range of benefits for healthcare to accommodate the human body's

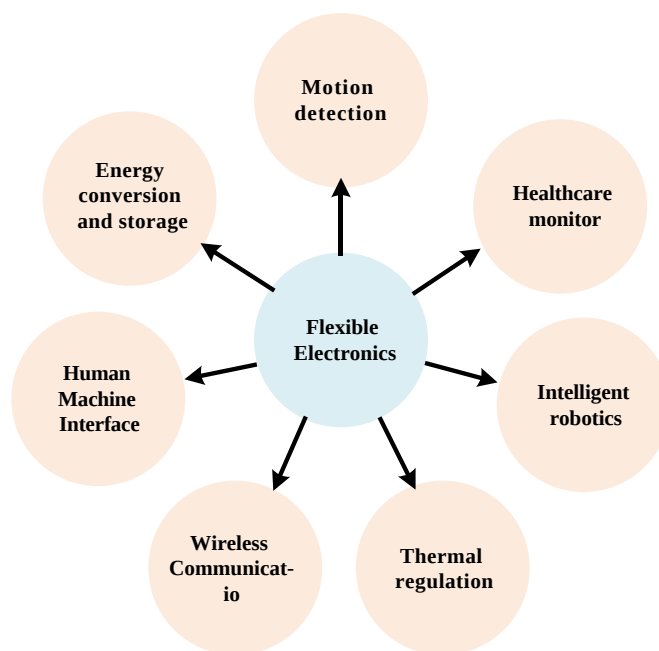


Fig. 4 Application of FE in various fields. Reproduced from Yu, H., *et al.*, 2021. An integrated flexible multifunctional wearable electronic device for personal health monitoring and thermal management. *Sens. Actuators A Phys.* 318, 112514. doi:10.1016/J.SNA.2020.112514.

imperfections to a significant extent and are excellent for continuous monitoring (Van Den Brand *et al.*, 2015). The use of sensors to track the wearer's physiological needs and health state in real time, as well as the incorporation of nanotechnology for improved performance, are just a few of the key applications of smart textiles in the healthcare industry (Barman *et al.*, 2022).

Flexible electronic skin

Electronics that are elastic, flexible, and capable of self-healing and imitating the functions of human or animal skin are referred to as "electronic skin." Many of the materials in this broad category include sensing properties that mimic how human skin might react to ambient changes in temperature and pressure (Wang *et al.*, 2013; Windmiller and Wang, 2013a; Chou *et al.*, 2015). Flexible clothing, medical monitors, and intelligent robots are just a few areas where an electronic skin with various sensor types can conduct and detect a variety of signals (Kim *et al.*, 2019; Lai *et al.*, 2018). Temperature sensors, stress sensors, and electrical-signal detectors are all integrated into one electronic skin (Chung *et al.*, 2019). A prototype of FE-skin that can detect contact pressure and multi-axis stresses was created using multi-layer tracks in elastomer matrixes. This sensor has dimensions of roughly 25 mm × 25 mm and a thickness of about 3.5 mm. The maximum strain that this sensor can withstand is about 250% (Zhao *et al.*, 2015). For sensitive tactile sensing, an antimicrobial, transparent electronic skin has been developed in Zhu *et al.* (2021) due to increasing attention toward triboelectric nanogenerator (TENG) ES (Cai *et al.*, 2022). TEG-based electronic skins have a diverse range of amazing applications and also have a great deal of promise for fine texture recognition (Zheng *et al.*, 2020; Yang *et al.*, 2013). A FE-skin based on TENG that mimics the morphology of human fingerprints to respond to tiny textures was developed in Zhao *et al.* (2021c). The lowest size of the texture that can be distinguished is as low as 6.5 μm, and the FE-skin can detect changes in the contact area brought on by the dynamic interaction between the fingerprint structure and the tested item surface. This electronic skin allows for the functionalities of distance resolution, multi-tactile sensing, and trajectory recognition and may be mounted conformably to any curved surface. In Cheng *et al.* (2022), for motion sensing, healthcare monitoring, and tactile identification, a triboelectric e-skin is created that is elastic, flexible, self-healing, environmentally stable, and long-lasting. The near-field electrohydrodynamic direct-writing approach was used in Luo *et al.*, 2021 and Dong *et al.*, 2021 to create an exceptionally sensitive FE-skin constructed of composite TF, which has the role of sensing pressure with great sensitivity and rapid reaction.

Energy harvesters

The development of ecologically friendly technology to harvest and store energy from the environment has been prompted by rising energy demand, diminishing fossil fuel supplies, and environmental concerns. Owing to the growing global requirement for substitute energy, there are several possibilities in the area of sustainable energy production from ambient mechanical energy sources, such as body motions. To transform this ambient biomechanical energy into electricity, recent advancements in energy harvesting technologies based on piezoelectric nanogenerators (PENGs) and TENGs have been produced (Fan *et al.*, 2016; Bagherzadeh *et al.*, 2022). Some of the techniques that have been used rely on taking advantage of environmental forces like temperature gradients for the creation of thermoelectric harvesters (Lineykin *et al.*, 2021; Peng *et al.*, 2022) and mechanical strain for the development of piezoelectric harvesters and finally, charging processes during friction for the development of triboelectric harvesters (Zhao *et al.*, 2021b; Zhao and Ouyang, 2021). Through the creation of piezo-potential when the electric symmetry in

the crystal structure is violated by the application of an external load, piezoelectric materials can transform mechanical energy directly into electricity (Wu *et al.*, 2016, 2021a).

The difficulty that the most advanced bio-devices necessitate outmoded heavy batteries, which prevent device downsizing and lifespan, is prompting a dramatic uptick in research on self-powered bio-electronics. The ability to convert mechanical energy into electrical energy, made possible by flexible piezoelectric materials, has greatly increased interest in harvesting mechanical energy from organ and human motions. An efficient, one-step method for fabricating large, lightweight, flexible piezoelectric energy harvesters made entirely of inorganic materials, based on special two-dimensional mica substrates was reported in Wang *et al.* (2018). Flexible piezoelectric energy harvesters using graphene oxide nanosheets were presented in Wu *et al.* (2021b), and they produced an output voltage and current of 60 V and 8 A during the finger bending-releasing process by harvesting mechanical energy from human body movements.

Flexible energy storage and conversion devices

SCs, lithium-ion batteries (LIB), supercapacitors, NGs, and zinc-based batteries are all examples of energy conversion and storage. Due to the distinctive electrochemical properties and configurational simplicity, supercapacitors and metal-ion batteries have become the two main technologies for stretchable and flexible energy storage (Wang *et al.*, 2020). The stretch-ability and flexibility of energy storage appliances are significantly influenced by the configurational design. Designs in 1D and 3D combinations have been established to satisfy the needs for aesthetics and other specific applications (Lu *et al.*, 2018). Because of the safety and high-specific energy, flexible and stretchy zinc-air batteries (ZABs) are thought to be the most expected power source for commercially available FE. The most recent developments and optimization ideas for flexible ZABs were discussed in Li *et al.* (2022). Advanced energy-efficient systems of phase change materials (PCMs) for latent heat thermal energy storage have been extensively investigated in Shi *et al.* (2021). Flexible PCMs are a novel class of substances with significant potential for usage in a diversity of smart appliances because they can withstand some deformation and can form dense contact with objects. Following the development of conventional SCs, the development of SCs depending on flexible substrates develops a prominent topic. Flexibility of Si SCs was first proposed in 1967 (Crabb and Treble, 1967) to diminish their thicknesses and to replace conventional solid substrates with flexible plastic substrates for flexible Si solar arrays. Over the past few decades, flexible SCs have drawn countless interest from both industry and academia owing to their extensive advantages of being lightweight, foldable, affordable, and having a wide range of uses (Zou *et al.*, 2010). The detailed analysis of PV technologies, which include DSSCs, organic SCs, and flexible perovskite SCs was presented in Fu *et al.* (2018). The requirement for carbon nanomaterials such as fullerene, graphene, and carbon nanotubes for PV applications was also outlined.

Challenges

FE technology is still difficult to make and takes a long time to complete. As it is becoming a promising aspirant for multi-functional and highly-sensitive sensing zone, and is attaining probable applications in innovative human-machine interface appliances, robots, healthcare monitoring, and prosthetics fields, an straightforward fabrication and inexpensive technique is required (Wu, 2019). In order to meet the increasing expectations brought on by huge numbers of consumers due to the benefit of flexibility, lightweight design, dependability, and sensitivity, research into wearable electronic gadgets has become an unstoppable trend. The major complexity associated with FE is that the entire electronic system needs to support stretching in addition to bending (Wu, 2019). Another difficulty in creating these electronic devices is how to shape the flexible conductors, especially when employing direct printing approaches (Wu, 2017). To make stretchable electronic devices, mechanical compliance is crucial, and products shouldn't be physically harmed or have their performance change when bent or stretched.

Because of the organic material's exceptional inherent compatibility, flexibility with stretchable substrates, and straightforward manufacturing procedures, organic materials are frequently used in FE. The electrical characteristics and stability of electronic gadgets that utilize organic substances must require extra improvement by straightforward chemical modification (Mirshojaei Hosseini and Nawrocki, 2021; Wang *et al.*, 2021). Advanced cellulosic materials for flexible electrical devices have come a long way, but there are still some problems that need to be solved. Existing cellulose-based electronics often only have single-function and don't integrate multi-functions, which restricts their possible applications, degrades performance stability, and decreases customer satisfaction (Zhao *et al.*, 2021a).

The development of practical, dependable wearable sensors that are suitable for everyday usage by the general public still faces significant obstacles. One of these limitations is the absence of suitable techniques for the seamless integration of electronics and wireless transmitters into the sensor package, which would result in truly functional and versatile monitoring devices. Further advancements in the fields of FE and printed electronics, sweat collection, and the electrochemical transduction of biomarkers are all required in this regard (Windmiller and Wang, 2013).

Although significant advancements in the domain of FE have been noted over the previous few centuries, significant work is still needed to expand their capabilities in order to fulfill the required characteristics in a diversity of applications like healthcare, fitness, energy harvester and military applications.

Conclusions and Future Outlook

FE and associated manufacturing technologies are currently developing quickly as a result of wearable electronics applications that have a favorable impact on many parts of daily life. The study into flexible devices has been substantially aided by the construction

of manufacturing techniques, which has accelerated the development of flexible devices. This article serves as an overview of FE that includes the structural design, extensive analysis on flexible materials and particular applications. The previous six decades of FE history and chronological development are summarized. This clarifies the basic design of the FE, its general characteristics, and the choice of flexible materials needed to offer the appropriate flexibility for particular applications. The advancement of flexible technologies for tracking bodily activity and monitoring one's own health, energy harvester, energy conversion and storage, emphasizing various polymer composite materials and unique, varied shapes structures is reviewed in this study. wearable electronic textiles in biomedical and healthcare.

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Study of Cadmium Zinc Telluride Thin Film Characterization Fabricated From Two-Source Evaporation Method

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Abstract

Thin film coating technology has leveraged different characteristics of an element deposited on a substrate by altering or improving its performance. The improvements in transparency, scratch-resistant, conductivity of electricity, transmission of signals, durability, which are typical in applications such as optoelectronics. Cadmium telluride is the most common photovoltaic material used in the market. Considering improved efficiency, Cadmium Zinc Telluride (CdZnTe) thin films are the materials of choice for several critical applications including radiation detector, solar cell, electro-optic modulators, etc., CdZnTe is a ternary alloy semiconductor solid solution of the II-IV compounds that has attracted researchers due to the wide tunability of its characteristics that include direct optimal band gap, high electro-optic coefficient and transparency in mid-infrared region. Depending on the applications, in recent times, CdZnTe films are obtained by evaporation, deposition, chemical synthesis, etc., for properties including, high resistivity, current-voltage characteristics, good mobility, long term sustainability, homogeneity and crystalline perfection. These are heavily dependent upon the crystal growth, synthesis methods, fabrication steps and purity of source raw material. This review presents a summary of CdZnTe thin films deposited by two-source thermal evaporation technique and subsequently the characteristics exhibited by such films.

Introduction

Thin film coating, an ubiquitous technology in today's world, has been present since 1880 when sputtering for optical coating was carried out successfully. Thin films grown from vapor phase can be traced back to 5000 BCE when metal layers were found on mud pots near metal ore extraction sites (Greene, 2014). Johan Schroeder, a German pharmacist, attempted a method for reducing arsenic oxide with charcoal through endothermic reaction, in 1649, which stands as the earliest reported work for thin metal film growth using vapor phase (Dwivedi, 2015). Similarly, with the advent of vacuum and electrical technologies, vapor deposition was developed, around 1852, by sputtering technique, while two decades later thermal evaporation technique was developed by Josef Stefan, an Australian physicist (Mitrovic, 2012). Radio frequency glow discharges was reported as early as 1890 with significant development of the technique observed in 1940 onwards (Winchester and Payling, 2004) for chemical analysis. However, only in 1966, John M. Blocher of Battelle Columbus Laboratory distinguished the deposition techniques by employing chemical reactions with that of sputtering and thermal evaporation, thus classifying the former as chemical vapor deposition (CVD) (Blocher, 1973) and later as physical vapor deposition (PVD) (Greene, 2017). Thin films of binary and ternary compounds are deposited through PVD, CVD or chemical solution deposition techniques. The choice of the technique depends on the selection of the raw material and its purity. Physical vapor deposition (PVD) methods are widely used for their robustness in term of using an appropriate target materials, process control and thus properties of thin film produced results in superior performance. PVD uses either thermal evaporation or sputtering technique to deposits the material of choice as a thin film on a substrate. Both these techniques produce thin films that have the capability to harvest energy by converting light to electric energy, and in other applications (Zheng, 2008).

Over the past several decades, the energy needs have skyrocketed due to population rise and consequently thriving automobile and other industries. Conventional sources including fossil fuels are fast depleting and pollute the environment with greenhouse gases. Therefore, alternate energy sources are much sought after and researchers are searching unconventional, renewable sources and innovative solutions to tap such scarce sources. Such solutions are expected to partly augment the energy supply, and in the long run replace the dependence on fossil fuels, while meeting high standards of human life as well as the sustainability and profitability of industries.

Renewable energy such as solar energy is fast becoming a source of energy to augment the energy supplying grids that also deals with the pollution problems. To effectively harvest such renewable energy, technologies including photovoltaic, thermos-photovoltaic, concentrated solar power, are being developed by researchers. Solar selective metamaterial absorbers are required for thermo-photovoltaic (Bilokur *et al.*, 2019) and concentrated solar power devices (Li *et al.*, 2015) to reduce the thermal loss and improve the efficiency. The solar selective metamaterial should possess good thermal stability in order to safely convert solar energy to heat for such applications (Chirumamilla *et al.*, 2020). Hybrid systems, involving photovoltaic/thermal, photovoltaic/thermoelectric, photovoltaic/concentrating solar power, etc., are also investigated as solutions to harvest energy over a wide band of temperature (Chauhan *et al.*, 2018; Gu *et al.*, 2019; George *et al.*, 2019). However, the system components are many and there performance and sustainability significantly affect the energy harvesting operation. Hence, in this review, one of the promising and prominently used thin-film photovoltaic semiconductor, ie, cadmium zinc telluride, used for energy conversion is considered.

Photovoltaic (PV) is a direct, efficient light to electricity conversion mechanism at the atomic level widely investigated by researchers. The shorter wavelength photons from solar irradiance are absorbed PV semiconductors releasing electrons and directly generate electrical current. However, the longer the wavelengths the photons are less energetic and hence, cannot excite electrons for separation, therefore converting it to heat. As a consequence, the PV semiconductor temperature increase thus reducing its conversion efficiency. Several materials are used to convert solar energy to electricity, based on the application, manufacturing

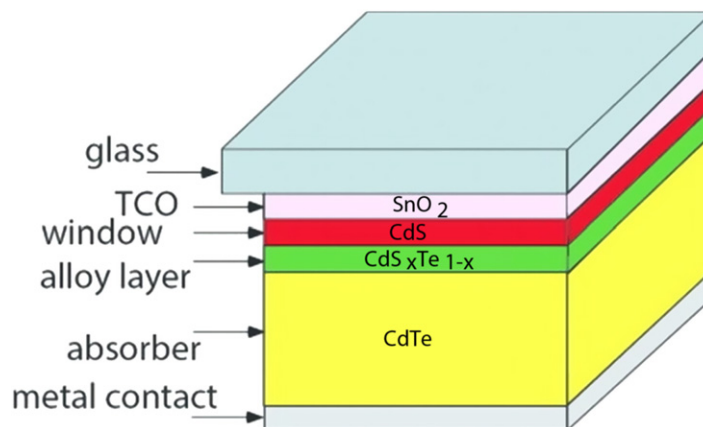


Fig. 1 Schematic of a CdTe photovoltaic cell. Reproduced from Corkish, R., 2013. Solar Cells", in Reference Module in Earth Systems and Environmental Sciences. Elsevier. Available at: <https://doi.org/10.1016/b978-0-12-409548-9.01481-0>.

route and conversion efficiency. Indium and Tellurium are rare while cadmium is abundant, however, it is toxic. Hence, in recent times, combinations such as, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe), and $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) absorbers are fast replacing conventional materials for thin-film PV as these materials possess promising optoelectronic properties and the use of nontoxic, earth-abundant elements.

Cadmium telluride (CdTe) has been promising candidate for solar cell applications as it, as a thin film of $2\text{ }\mu\text{m}$, can absorb almost all of incident solar radiation (Afzaal and O'Brien, 2006). Hence, it is one of the few II–VI compounds widely used photovoltaic devices (Patidar *et al.*, 2006). CdTe has a band gap of $1.45\text{--}2.08\text{ eV}$ which is tunable (Trivedi *et al.*, 2021), and has excellent light absorption in the near infrared range (Ai *et al.*, 2022), (light absorption coefficient $\alpha > 104\text{ cm}^{-1}$) for the visible solar spectrum (Caglar *et al.*, 2006; Ferekides *et al.*, 2000). One of the advantages of this material is the possibility to vary its band gap with various dopant concentrations, like tin (Arivarasan *et al.*, 2022), silver (Venkatachalam *et al.*, 2023), and others elements (Al-Douri *et al.*, 2010; Fahrenbruch, 1977) for improved light absorption efficiency.

CdTe-based PV cells are made using thin-film technology with few micron thickness active layers. A schematic diagram of a typical CdTe solar cell is shown in Fig. 1.

The photovoltaic cell consists of a substrate on which layers of other materials are deposited. Transparent and colorless thin film of conducting oxide (TCO) layers, such as Indium tin oxide, tin oxide (SnO_2) or Cd_2SnO_4 allow visible light and are highly conductive to transport current efficiently. Intermediate layers, such as cadmium sulfide (CdS), in the range of $10\text{--}500\text{ nm}$, helps in both the growth of further layers and electrical properties between the TCO and Cadmium Telluride (CdTe). The CdTe thin film is the absorber layer that acts as the primary photoconversion layer, absorbing most visible light within the first micron of the material. Together, the TCO, intermediate layer and CdTe, forms an electric field that converts light absorbed in the CdTe layer into current and voltage. Metal contact is placed at the other end to form the electrical contacts.

However, CdTe thin-film has several limitations, including, complexity in the making, increased protection in the outdoor for long-lasting operation, etc., in addition to toxicity, limited tellurium supply, and less efficiency compared to silicon films. The solar conversion as well as radiation detector efficiency can be improved by adding intermediate layers of CdZnTe and increasing the doping concentration to the photovoltaic structure (Neda Rezaie *et al.*, 2015).

CdZnTe (CZT) is a compound semiconductor with a tunable direct band gap of $1.4\text{--}2.26\text{ eV}$ and hence it is a promising material for solar cells and other optoelectronic devices. Cadmium zinc telluride (CdZnTe) has a cubic, zinc blende-type lattice structure with atomic numbers close to that of CdTe and a density 3 times that of Si. Addition of a few percent of zinc to the CdTe melt results in an increased band gap as well as energy of defect formation. This in turn increases bulk resistivity and reduces the dislocation density, resulting in lower leakage currents. Although, CdZnTe has many attractive properties it also suffers from some serious drawbacks. For instance, compared to the elemental semiconductors, it has a far high defect density, resulting in a large number of trapping sites. This leads to both uniformity and stability problems and in fact, leakage currents are dominated by these defects rather than the band gap. The large number of trapping sites also ensure that the transport properties of carriers in CdZnTe are far inferior to those of Si and Ge and because of this detector sizes are limited. The problem is exacerbated by the fact that the transport properties of the electrons and holes are markedly different. Typically the mobility-lifetime products of the holes are $10\text{--}100$ times worse than that of the electrons. The lifetime of charge carriers is limited either by trapping and recombination at deep levels or by band-to-band recombination due to a strongly elevated concentrations of free electrons and holes at high fluxes of X-ray photons (approx. $10^{10}\text{ cm}^2\text{ s}^{-1}$) compared to detectors working at low fluxes.

CZT thin films are deposited by various methods like closed-space sublimation, electro-deposition, liquid phase epitaxy, molecular beam epitaxy, laser ablation, thermal evaporation, etc. However, researchers prefer to use thermal evaporation method as it is found a better choice due to fact that the high rate of targets precursors utilization, low cost, excellent reusability and stability of the films.

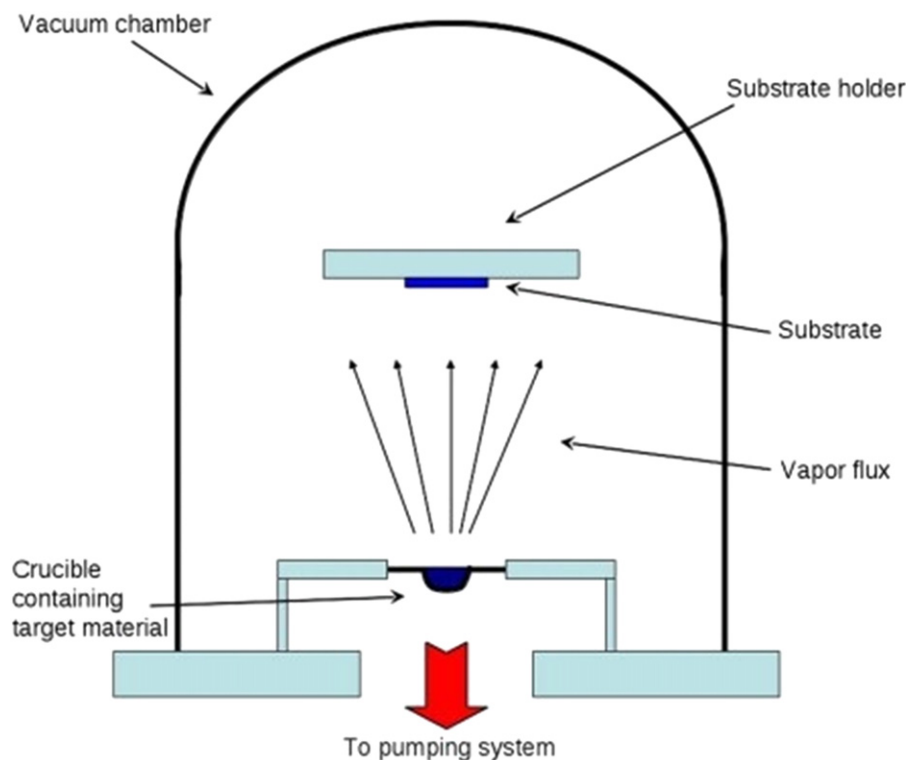


Fig. 2 Single source thermal evaporation equipment. Reproduced from Martín-Palma R.J., Lakhtakia, A., 2013. Vapor-Deposition Techniques"; Engineering Science and Mechanics Materials Research Institute (MRI). Available at: <https://doi.org/10.1016/B978-0-12-415995-2.00015-5>.

Thermal Evaporation

Thermal evaporation technique is simple and useful in many engineering applications in recent times. It is used commonly in thin film deposition due to the process simplicity, cost effectiveness and scalability (Su and Sha, 1995). Thermal evaporation is a physical vapor deposition technique in which the material is heated in vacuum until the surface atoms has sufficient energy to leave the surface. The atoms travels across the chamber to coat the substrate kept at a distance of 150–1000 mm. The thermal energy of the atoms will be less than 1 eV.

The chamber is made hemispherical for uniform deposition and the source material is held as powder or solid bar in a boat or resistive coil, respectively. The source material is heated either by resistive or inductive heating or by electron beam and evaporated. In order to achieve high melting point, a large direct current and high vacuum is used that assists metal evaporation, migration and condensation on the substrate, forming a thin film coating. The schematic of the thermal evaporation process is given in Fig. 2.

The metal deposition rate depends on the vacuum pressure, temperature of the source material and the substrate, and atomic mass of the source material. A detailed description of thermal evaporation process is reported by Levy (2016). The important performance indices of thermal evaporation are as follows,

- Deposition rate
- Film Uniformity
- Film conformity
- Structural properties – microstructure, lattice arrangement, grain size, orientation, etc.,
- Electrical properties – resistivity, dielectric properties, etc.,
- Mechanical properties – residual stress, adhesion, yield strength, etc.,
- Optical properties – transparency, refractory index, optical band gap, etc.,

The main limitations with thermal evaporation is that the step coverage and geometric conformity is poor as the direction of migrating vapor dictates the deposition pattern and the thickness may vary depending on the evaporation chamber geometry. The step coverage is poor with least or no deposition in the vertical surfaces. In order to alleviate this non-uniformity, the substrate is heated or mounted on a rotating planetary. This thickness variation and poor film morphology can strongly limit PV performance of the active absorbers, particularly for films. Therefore, it is crucial to develop robust methods for growing high-quality thin films with high crystallinity and minimal pinhole densities. One potential approach to achieve this is to use co-evaporation, which has successfully led to the growth of high-quality materials (Chen *et al.*, 2015; Lin *et al.*, 2015; Liu *et al.*, 2013; Malinkiewicz *et al.*, 2014; Khazaei *et al.*, 2018).

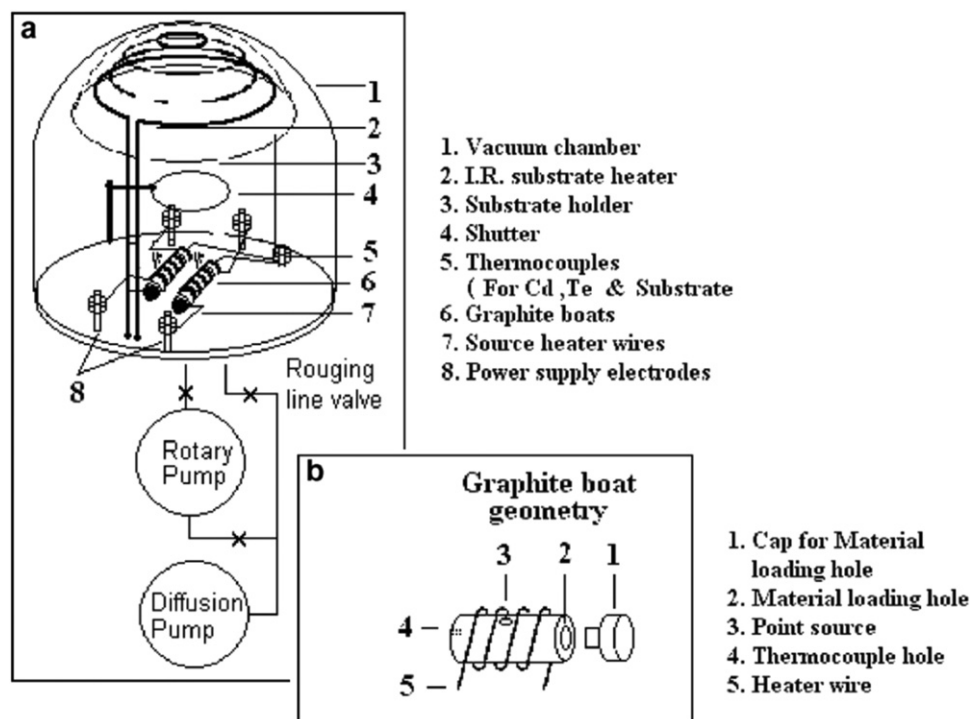


Fig. 3 Two source evaporation method. Reproduced from Alamri, S., Khushaim, M., Alamri, S., 2021. "Preparation and characterization of $\text{Cu}_2\text{ZnSnS}_4$ thin films with various compositions deposited by a dual thermal evaporation technique". *Journal of Alloys and Compounds* 870, 159392.

Two Source Thermal Evaporation

Thermal co-evaporation is a suitable technique for bi/multi-layer thin film deposition or alloy preparation where the composition dependent property can be tuned to the required level by taking the source material in stoichiometric ratio (Sahana *et al.*, 2020). The compositional change is accompanied by corresponding changes in structural and optical properties, which is also essential in material designing to achieve most suitable material for heterojunction devices. However, these compositional changes are highly sensitive to the source material's evaporation behavior and therefore, challenging to control the formation of other phases.

Alamri *et al.* (2021) used the experimental set up (dual-thermal evaporation technique), shown in Fig. 3, to deposit $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films with Cu-rich, Zn-rich, Sn-rich, and S-rich material source compositions. The stoichiometric ratio of the source compositions plays a significant role in the physical properties of the thin film deposited. The estimated band gap (E_g) was found to vary between 1.53 and 2.3 eV for the as-deposited films. Zn-rich film recorded the maximum transmittance of 60% (at a wavelength of 600 nm) and Cu-rich film recorded the least transmittance of about 14%. Near-stoichiometric CZTS film and Sn-rich films recorded an intermediate spectral transmittance. The authors observed that Zn-rich film produced high homogeneity and low surface roughness and hence recorded the maximum transmittance even with a high thickness value. However, the Cu-rich film recorded minimum transmittance, even with the lowest thickness. Annealing the films increased their transmittance, significantly in Zn-rich film and moderately in Cu-rich film, as shown in Fig. 4.

The transmittance of the annealed Zn-rich film exhibited a relatively high transparency of 85% at wavelengths greater than 675 nm. The increase in the transmittance in annealed films may be due to the re-evaporation of the sulfur from the films and an increase in the crystallinity. The optical reflectance properties of the as-deposited films were found to be varied, with Cu-rich film alone exceeding 50% in the region above the material band gap. However, annealing of the films resulted in decreasing the reflectance that can be attributed to increased surface roughness, as a result increased light scattering (Okwako, 2013). The near stoichiometric film produced the least reflectance in both as-deposited and annealed conditions. Due to these optical properties, the highest band gap was observed in Zn-rich film (2.3 eV) followed by near stoichiometric film (1.9 eV).

Several other authors have investigated dual source evaporation method for depositing stoichiometric ratio of preferred materials on the chosen substrate. As the evaporation process involves four stages, namely, (1) evaporation of the source material, (2) transportation of the vaporized atoms from the source material, (3) reaction with similar, vaporized second source material and (4) deposition and diffusion of the combined material on the substrate. Surface modification and growth can be modified by varying process parameters such as evaporation temperature, temperature of the substrate, substrate material, etc., (Kun Zhang *et al.*, 2018). With increased deposition time, the surface morphology becomes smooth and the defects reduced. When the substrate is at room temperature the particles condense immediately on the surface. Moderately higher substrate temperature than room temperature enables thorough mixing and diffusion of the film in the substrate. By varying the power for individual source

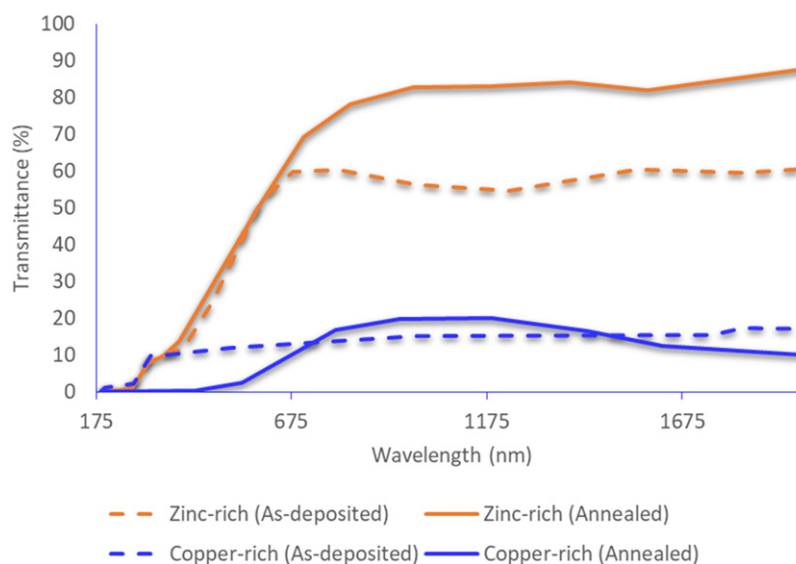


Fig. 4 Comparison of transmittance spectrum. Reproduced from Alamri, S., Khushaim, M., Alamri, S., 2021. "Preparation and characterization of $\text{Cu}_2\text{ZnSnS}_4$ thin films with various compositions deposited by a dual thermal evaporation technique". *Journal of Alloys and Compounds* 870, 159392.

material the deposition rate and film thickness can be varied. However, film deposited at high substrate temperature introduce residual stress due to coefficient of thermal expansion of the source material (Lee, 2001). Appropriate parameters and order is essential to reach stoichiometric composition and resulting opto-electric properties (Choudhari *et al.*, 2022).

CdZnTe Thin Films Characteristic Properties

The performance of single crystal CdZnTe radiation detectors is dependent on both the bulk and the surface properties of the material (Prettyman *et al.*, 2001). The layer thickness was found to be independent of exposure time. Chen *et al.* (2017), investigated the response of CdZnTe to 14.1 MeV neutrons, experimentally. CdZnTe crystals were grown using vertical Bridgman method and CZT film response to the pulsed X-ray, with a sampling rate of 5 G/s under a working voltage of 300 V were recorded. The relative position between the pulsed X-ray source and the detector, the space angle of the detectors to the target and the calibrated sensitivity of the detector significantly influence the detector response. They found that the detectors maintain a stable response until a maximum dose rate of 10^6 neutrons/($\text{cm}^2 \cdot \text{s}$) and accumulative dose of 10^{10} neutrons/ cm^2 .

Chen *et al.* (2010) used multi source evaporation of organic film, arranged in circular patterns of different diameters for large scale deposition. Uniformity in the film thickness, shown in Fig. 5(a), and hence the roughness of the film decreased up on increasing the distance between the source and substrate. As the source circle radius and number of sources increases, the film uniformity increases marginally, shown in Fig. 5(b), compared to effect of source-substrate distance.

The surface roughness decreases with increase in the number of sources $R_a = 4.94$ for two sources & $R_a = 4.66$ for three sources), and keeping the sources symmetrically helps compensate for peaks and valley, reducing the thickness variation. A single evaporator, three chamber, two source material evaporation system was used by Pardo González and Torres (2018) for ZnTe and ZnSe deposition. ZnTe and ZnSe are subjected to simultaneous sublimation and mixed in a chamber before depositing the ternary compound ZnSeTe thin film on the glass substrate. The lattice parameter reduced, from 6.0806 Å to 5.7413 Å, as the substrate temperature is increased, falling between the lattice parameter of ZnTe and ZnSe, respectively. The transmittance spectra indicates decreasing refractory index due to increased Te concentration in the sample.

Prasada Rao *et al.* (1996) used two source vacuum evaporation technique to deposit CdZnTe film, using 5 N pure CdTe and ZnTe source compounds. The lattice parameter of the CdZnTe films evaluated from the XRD spectra were found to be decreasing from 6.484 Å for $x = 0$ (CdTe) to 6.104 Å, for $x = 1.0$ (ZnTe). The optical transmission spectra of CdZnTe films recorded at room temperature in the wavelength range 700–2000 nm with high transmission of about 75% in the higher wavelength region, shown in Fig. 6, and sharp absorption edges were observed in the films.

The reflection spectra of the CdZnTe films recorded in the wavelength region 185–400 nm at room temperature along with the band structure and the proposed transitions. The optical properties of ZnTe deposited by co-evaporation of high purity Zn and Te as the source materials was investigated by Akram *et al.* (2000). Te was found to evaporate faster than Zn and it requires a lower temperature to evaporate. The high-frequency dielectric constant was found to increase with grain size of the films, together with a slight increase in the band gap. Annealing the films enhances the opto-electronic and detector properties for X-ray and gamma ray detection (Yang *et al.*, 2013). Wanwan *et al.* (2006), created a model correlating the resistivity of CdZnTe crystal grown by vertical Bridgman method followed by annealing to the diffusion coefficient. From the experimental data, the diffusion coefficient decreased with increasing temperature. The Cd

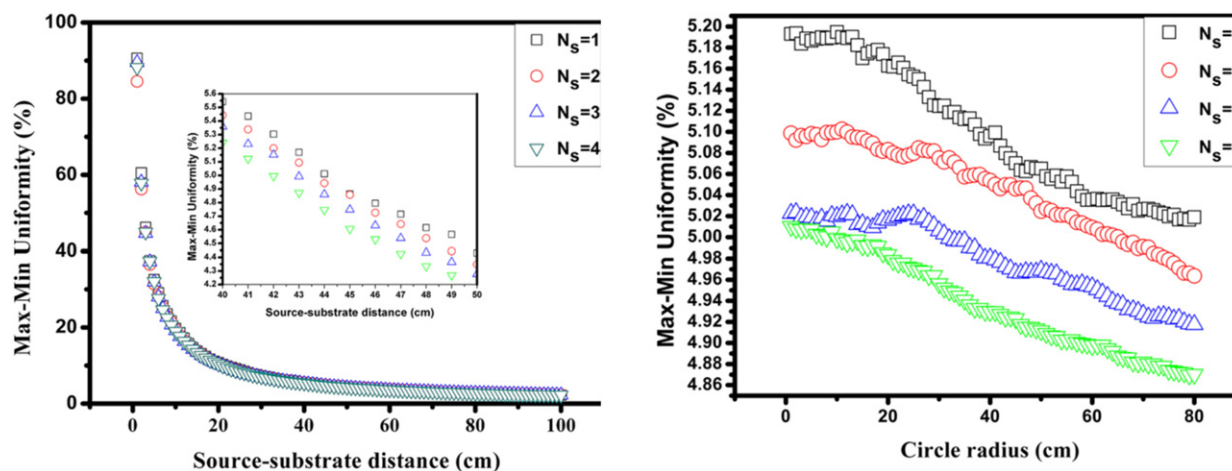


Fig. 5 Film thickness uniformity variation, (a) based on Source-substrate distance, (b) based on Circle radius. Reproduced from Chen, H., Gang, Y., Wenbin, C., Kaijun, L., Feng, L., 2010. "Simulation of the organic thin film thickness distribution for multi-source thermal evaporation process". Vacuum 85, 448–451.

evaporation, during crystal growth, creates a certain number of vacancies (V_{Cd}) which decreases the resistivity of the crystal. Annealing the film in Cd vapor compensates these vacancies with the formation of Cd interstitial donors and subsequently by the free electrons released due to ionization.

The electrical properties and UV response of polycrystalline CdZnTe thick films grown SnO₂:F coated glass substrate by close-spaced sublimation method was investigated by Zhang *et al.* (2015). The films were 270 μ m thick with 30 μ m average grain size. The CdZnTe films were subjected to Br-MeOH etching and ZnCl₂ annealing. The Br-MeOH etching improves UV light sensitivity while the ZnCl₂ annealing process does not improve the electrical property. Watanabea *et al.* (2003) investigated the idea of stacking layers of CdTe to achieve better energy resolution and higher efficiency for gamma ray detector application. Increasing the thickness of the CdTe decreases the charge collection performance which degrades the energy resolution and lower detection efficiency. With a 10-layer detector, Cobalt radioactive source located at 5 cm distance was measured with an accuracy of 1–2 mm, while a 40-layer detector can capture neutron in the energy range of 500 keV up to 6 MeV, with an energy resolution of 20 keV. The coplanar anode geometry on the detector performance in depth sensing was investigated by He and Sturm (2005) and found that Generation 3 coplanar grid design has improved performance with a consistently good energy resolution of 2.0%–2.1% FWHM at 662 keV.

Owensa *et al.* (2006) conducted series of experiments to determine thick CdZnTe detector response to X- and gamma ray and found to be linear over the energy range of 10–100 keV. The FWHM energy full-width at half maximum resolution was observed to be varying for pencil beam illumination and full area illumination, indicating the degree of non-uniform crystallinity and stoichiometry in the bulk material. The rise time discrimination (RTD) was used to filter out events due to holes. The shape of photopeaks can be substantially improved at high energies, however, at the expense of photopeak efficiency. They found that a very good performance can be obtained by combining low-noise front-end architecture and RTD below 100 keV, but other techniques such as bi-parametric corrections or single carrier sensing techniques shall be used to maintain spectrometric performance. Won *et al.* (2008) investigated the X-ray sensitivity of semi-insulating polycrystalline Cl-doped CdZnTe thick films. Electric field, mean photon energy, film thickness, charge carrier transport are some parameters studied and compared with other detector materials including HgI₂, PbI₂, a-Se. The X-ray sensitivity of CdZnTe:Cl was found to be higher than the other detector materials, 7–20 times more in the case of a-Se depending on the electrode preparation.

Numerical simulation studies to predict the lifetime of charge carriers and its influencing factor, especially at high X-ray fluxes (Franc *et al.*, 2011). The simulation results indicate that at standard operating conditions the Shockley–Read recombination is dominant, independent of the radiation energy. This gives the researchers an opportunity to increase of lifetime of carriers and charge collection efficiency through material improvement.

Effect of Doping

The effectiveness of semiconductor depends on its ability to dope with impurities to change its properties, usually to p- or n-type. For CdTe, CdSe, CdS, ZnSe and ZnTe to be used in photovoltaic solar cells, they must be doped. ZnSe, CdSe and CdS can be easily doped only on n-side, while ZnTe and few other newly synthesized II–VI compounds only on p-side (Desnica, 1998). The advantage of Cd is that, it can be easily doped to reasonably high concentrations of both types (Oudhia *et al.*, 2010) p-type and n-type. This property of Cd is useful in making homo- and heterojunction devices. Silver (Ag) may be incorporated as an acceptor in the II–VI semiconductors, since it influences the electrical conductivity as well as optical properties of these materials (Shah and Mahmood, 2013). Magnetic elements can be introduced into nonmagnetic II–VI semiconductors to make them magnetic. This category of semiconductors, called diluted magnetic semiconductors

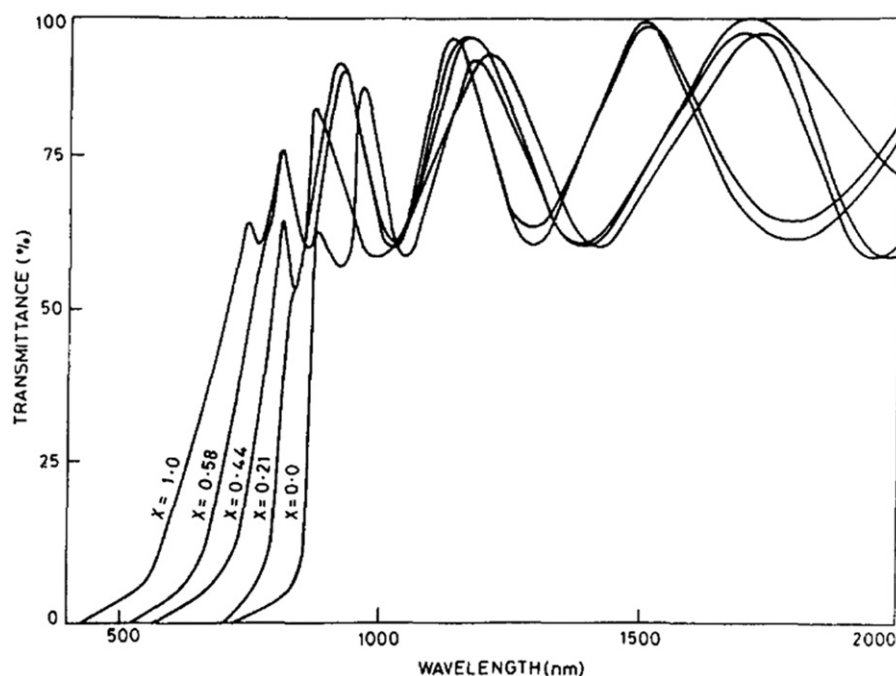


Fig. 6 Transmission spectra of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films. Reproduced from Prasada Rao, K., Md Hussain, O., Reddy, K.T.R., *et al.*, 1996. Characterization of two-source evaporated cadmium zinc telluride thin films. *Optical Materials* 5, 63–68.

(DMS), consists of alloys of nonmagnetic semiconductor and magnetic elements. The study of DMSs and their heterostructures have centered mostly on II–VI semiconductors, such as CdTe and ZnSe, in which the valence of the cations matches that of the common magnetic ions such as Mn (Merciline *et al.*, 2010). It has also been shown that ZnO doped with cobalt and other transition metals exhibits –under certain conditions– dilute magnetic semiconductor (DMS) behavior with high Curie temperature (Ohno, 1998). Olsson *et al.* (2008) proposed an improved photovoltaic conversion characteristics by introducing ferromagnetic impurity to make diluted magnetic semiconductors and reduce the non-radiative recombination rates.

Effective doping of wide bandgap II–VI compounds, both p- and/or n-type, is difficult to achieve and hence, the main obstacle in their photovoltaic applications. Doping limiting mechanisms in II–VIs are self-compensation by native defects or native defect–dopant pairs, chemical solubility limit of dopants, lack of appropriate shallow acceptors and donors, deactivation of dopants due to lattice relaxation and the limit imposed by the formation of a second phase (new compound) (Desnica, 1998).

There are no general rules for optimal doping of these compounds, but the solutions to the doping problem depend on the type of semiconductor and the technology available. The most promising approaches to solve the doping problems in II–VI compounds are non-equilibrium processes. Non-equilibrium processes like ion implantation and particularly low-temperature crystal growth such as molecular beam epitaxy (MBE) and vapor phase epitaxy (VPE) are the practical ways to transcend doping limits and obtain material suitable for various applications (Desnica, 1998). Advantages of the lower growth temperature are: first, reducing the possibility of the thermodynamic restrains and surpassing their limitations, and second, the lower concentration of compensating defects.

Doping of II–VI films can be accomplished by different ways such as: coating the substrate with a thin layer of the dopant before deposition or applying a layer of dopant after deposition (with a subsequent heat-treatment), and finally, incorporation of the dopant during the film deposition. The latter method appears to result in superior doping. Doping during chemical vapor-deposition has proved quite successful for many of the II–VI compounds (Thiyagarajan *et al.*, 2009). Doping can be done by using thermal evaporation as well as solution based methods like ion exchange method in the II–VI semiconductor thin films. The ion exchange is one of the most convenient methods for doping in the II–VI semiconductor thin films (Shah and Mahmood, 2013). Doping through the spray pyrolysis technique which can be accomplished by adding the doping compound to the precursor solution is easy and effective. Doping of polycrystalline films in general is complicated by rapid diffusion along grain boundaries. Impurity photovoltaic effect was also investigated and several authors found this method increases the efficiency in indium doped silicon solar cells (Par Olsson *et al.*, 2008). However, introduction of impurities may affect diffusivity and the device lifetime as indicated in ref (Sircar *et al.*, 2013).

Ternary systems such as $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ alloy are one of a few semiconductor materials which have a tunable bandgap and allows tandem solar cell to absorb a larger fraction of the solar spectrum energy (Reis *et al.*, 2009). Table 1 presents the common dopants used in semiconductor industry for different groups (Group II – VI).

Table 1 Doping elements and characteristics

Group - IIa, b	Group - III	Group - IV	Group - V	Group - VI
Be	B	C	N	O
Mg	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te
Hg	Tl	Pb	Bi	Po

Note: Reproduced from Faculty of Engineering - Kiel - Germany. Available at: www.tf.uni-kiel.de.

Applications

Major application of CdZnTe is in the radiation detection and second major application being solar cells. Radiation can be ionizing or non-ionizing, energy waves or high speed particles that are available in nature or man-made. Non-ionizing radiations include visible light, radio waves, cell phone communication waves, microwaves, etc. These are low-level radiations a human body can withstand on a day-to-day basis. Sustained exposure to high-level radiation, especially, X-rays, Gamma rays, Ultraviolet radiation, etc., can be detrimental to human beings that can damage cell structure and DNA. Nonetheless, X-rays and Gamma rays are types of ionizing electromagnetic radiations that are useful to mankind in many ways, including medical damage diagnostics, kill cancer cells in human tissue, as well as in manufacturing industries to identify defects, screening weapons of destruction at strategic locations, lithography in electronic industry to manufacture high density integrated circuits.

Of all these detection techniques, X-rays and Gamma rays are frequently tested by using Direct Conversion Materials in almost all applications in the current status. CdTe and CdZnTe are the materials of choice in the detector technology of recent times for X-rays and Gamma rays. Ensuring the long term stability of the contact to CZT is very important for detector applications, hence any improvement in the adhesion properties and reduced CTE mismatch between the electrical contact and CZT would be an added advantage. Also, other detector properties expected are: high resistivity, current-voltage characteristics, good mobility, long term sustainability, homogeneity and crystalline perfection. These are heavily dependent up on the crystal growth, synthesis and fabrication steps and purity of source raw material.

Spectroscopy grade CdZnTe has been utilized in several critical applications and the performance depends on mobility-lifetime products (Vincent *et al.*, 2002). The transport and collection of the photo-generated charge carriers, the carriers' drift properties combined with the applied electric field gives the drift length for electron and holes (Van Scyoc *et al.*, 1999; Marks *et al.*, 1999; Gliere *et al.*, 2000). The energy resolution of CdTe and CdZnTe detectors is poor as they suffer from poor hole collection. Modifications and correction methods to compensate for the hole trapping enhanced the energy resolution (van Pamelen and Budtz-Jorgensen, 1998; Shor *et al.*, 1999; He *et al.*, 2000); and Bale *et al.* (1999) investigated CdZnTe detectors by cooling below -30°C and found that the leakage current is reduced, significantly improving energy resolution. The detector performance was found to be linear and its size and cost has made it attractive for industries such as X-ray computed tomography (Ricq *et al.*, 2000), and perform X-ray spectroscopy on spent nuclear fuel, uranium solution and pellets for analysis (Abbas *et al.*, 1998) and astronomy and space exploration (Stahle *et al.*, 1999; van Pamelen *et al.*, 2000; Limousin *et al.*, 2000).

Another critical application worthy of CZT detector principle is to measure the intense and rapidly changing pulsed gamma ray flux in neutron and gamma mixed radiation field such as pulsed reactor, space radiation environment, etc. Important parameters, such as, time response, amplitude, and integral area, are calculated before and after irradiation with different accumulative doses of 14.1 MeV neutrons to determine their effects on the performance of the CZT detector (Chen *et al.*, 2017). Introduction of coplanar grid technique has a reasonable γ -ray response and good spectroscopic resolution. The hard X-ray and γ -ray detector response function was found to be linear over a wide energy range (Alan Owens *et al.*, 2006).

On the other hand, the micro-scale X-ray response mapping technique and 3D infrared (IR) transmission microscopy yielded clear evidence that high densities of Te inclusions can trap free charge-carriers generated by incident radiation, thereby entailing significant fluctuations in the total collected charge, and strongly degrading the energy resolution of thick CZT detectors. Post-growth annealing was found to improve the detector properties. Annealing CZT detector crystal in Cd rich environment effectively removes Te and loss of resistivity. Te migration was also observed during temperature gradient annealing (Yang *et al.*, 2013).

Discussion

Thermal evaporation technique, originally devised by Faraday in 1852, has since been developed into a variety of techniques to deposit thick or thin film of material on a substrate. The bulk material to be deposited is heated by passing current on the crucible holding the material or through a heater filament. During this process, atoms or molecules are removed from the bulk material which traverses as a vapor flux through the chamber, typically in vacuum, and gets deposited on the substrate. One or more materials can be deposited forming single monolayer upto several microns thickness by tuning the process parameters. Using a rotary table for mounting the bulk material and rotating alleviates step defect in the coating and enables uniform deposition. The major advantage of using thermal evaporation technique for film deposition is that the generally available vacuum equipment can be used for the process.

Two source evaporation enables more than one material deposition on the substrate which allows the production of a wide range of compositions with unique and required properties. The sublimation rate depends on the source material and the deposition and thickness is controlled by various parameters, including, positioning and rotating the substrate, applied current, etc. Roy *et al.* (2017) used aluminum doped Zinc oxide (AZO) as interlayer between metal and CdZnTe thin film to alleviate the thermal stresses that develop due to the difference in their coefficient of thermal expansion (CTE). This non-metallic contact layer offers better adhesion and improved hardness, in addition to comparable CTE. Better adhesion is due to the oxide nature of AZO that ensure better chemical bonding at the interface and higher hardness is due to ZnO which is 8–20 times harder than the conventional metallic contacts. At lower applied bias (+1 to –1 V) both gold contact and ZnO contact has same current-voltage characteristics while the characteristics is quite different at higher bias voltages.

For an application such as X-ray or Gamma-ray detection, the deposition has to be superior producing high resistivity, good mobility-lifetime and homogeneity in the film. Hossain *et al.* (2013) demonstrated the deposition of Cadmium Magnesium Telluride in a vertical three-heat-zone tubular furnace using this zone melting to grow the crystal for X- and gamma-ray detector and compared its characteristics with the conventionally used Cadmium Zinc Telluride and Cadmium Manganese Telluride. Magnesium telluride possess high crystallinity and good homogeneity as the Mg segregation coefficient in CdTe is close to 1. Also, optimal energy band is attainable using less Mg compared to the amount of Zn and Mn needed in CdTe, creating less compositional related defects. They were able to achieve high-resolution detector response maps using a high flux X-ray beam, though with few bulk material defects. However, the limitation with magnesium is the risk of explosion as it often reacts exothermically during synthesis. Similarly, Babar *et al.* (2013) investigated the performance of single crystal CdZnTe sliced and subjected to chemical etching using bromine in methanol treatment. The performance, including charge generation, charge transport and intrinsic electric field, depends on the surface properties of the CdZnTe slice which in turn determines the radiation detection capacity {a,b,c}. The oxide layer thickness was determined using Beer-Lambert expression and photo electron take-off angle.

Zha *et al.* (2011) fabricated nano-crystalline CdZnTe films on silicon wafer by thermal vacuum evaporation (Modified Vertical Bridgman method). The CdZnTe films with a typical particle size of 15 nm, an effective band gap of 2.26 eV and an amorphous Te interfacial layer with a thickness of 3 nm was observed. The higher vapor pressure and desorption rate of Cd compared to Te enables Te to form the interfacial layer. Nasioka *et al.* (2015) studied the influence of gas-static processing on the properties of Au-CdZnTe-Au structures used in detector applications. The gas-static processing of the Au-CdZnTe-Au structures leads to a significant increase of the electric resistance of the structures; increase of the intensity of the photoelectric absorption peak when X- and gamma-radiation register energy near 32.19 keV. This is due to the formation of TeO₂ on the contact surface first, that causes low values of the leakage currents. Hansson *et al.*, (Conny *et al.*, 2014) presented a summary of the material developments pursued by European Space Agency for X-ray, gamma, and neutron detection. The choices and their specific advantages were identified and discussed. Si and Ge were the most commonly used detectors, however, the small band gap of Ge requires liquid nitrogen cooling system. This increases the payload which limits the operation duration, especially in space. In addition, low atomic number of these two elements lead to relatively low radiation detection efficiency. Compound semiconductors such as CdZnTe and thallium bromide (TlBr) have wider bandgap and higher atomic number. These materials can be operated at room temperature as the wider band gap reduces the thermally generated free carriers, thus eliminating the cooling system for their operation. The higher atomic number allows higher detection efficiency in the range of 10–100 keV. However, the morphological instabilities at the substrate-film interface capture Te from the melt droplet. Te inclusions cause degraded spectral response and polarization effects. Vincent *et al.* (2002) investigated the performance of CdZnTe for use as ancillary detectors for channel selection in nuclear spectroscopy. They investigated the response for a range of 2 MeV (alpha particles) to 13 MeV (protons) and found that proton penetrates around 70% deeper than the alpha particles at beam energies ranging from 400 to 1030 keV. The performance of the CdZnTe crystal is comparable to silicon detectors. The cost involved in producing such compounds (CdZnTe) is inexpensive and the photovoltaic effect can be tuned to the requirement, ranging from 1.4 eV to 2.6 eV (Ikhmayies, 2014). Two source evaporation method is found to yield superior deposition compensating for peaks and valleys resulting in high absorption efficiency.

Conclusions

Crystalline silicon and Cadmium telluride have been the potential material for solar cell and radiation detection applications. Silicon has the maximum light absorption efficiency, however, the cost is high compared to cadmium telluride while the latter has high absorption energy and low cost in manufacturing. Cadmium zinc telluride is an alloy of cadmium telluride that has an extended band gap of 1.4 – 2.26 eV. Two source evaporation method is found to be suitable for CdZnTe film deposition which can produce superior films that has high conversion ratio. It is a credible approach toward simplistic tuning of the band gap of the film for specific applications envisaged for such materials. The composition of individual material in CdZnTe can be adjusted by varying the applied voltage on the source material and hence achieve precise band gap energy. The optical properties are tunable and the optical transmission spectra of CdZnTe films is in the wavelength range 700–2000 nm with high transmission of about 75%. The structure of the film depends on the growth mechanism. Low and room temperature substrate produce close to equi-axial crystallite structure while high substrate temperatures lead to columnar grains. Hence, such CdZnTe thin films are appealing for precise and demanding applications such as solar cell and X-ray and Gamma ray detectors.

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Magnetostrictive Cobalt Ferrite, Nanoparticles Preparation and Magnetic Characterization

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Introduction

Magnetostriction is the observed change in physical dimensions of a ferromagnetic material in the presence of a magnetic field. This change in dimensions could be as shrinkage or an elongation. Moreover, the change in dimensions is the result of a change in magnetic field orientation of some of the magnetic domains in the material. These domains align with the externally applied magnetic field. This alignment is achieved by the unpaired electrons which move in orbitals around some of the atoms in these materials. These orbitals are non-circular, and their probability densities have defined geometric properties. Unpaired electrons in each of these orbital produces a magnetic field with specific magnitude and direction, and some orbitals enable the material to respond to the direction of the applied magnetic field better than other orbitals. Because the electrons in these orbitals are in incomplete shells, it is possible for them to switch instantaneously from one orbital to another, and so enable the material to respond to the externally applied magnetic field.

Because these electrons are the outermost electrons in each of the atoms concerned (the conduction electrons, if there are any, are not attached to the atoms at all) they also influence the distance between atoms; that is the distance with which one atom can approach a neighboring atom. The responses are complex, because these orbitals (in the 'd' shell in transitional elements, and in the 'f' shell in the rare earth elements) also interact with other orbitals (in the 'p' shell) which define the chemical properties of the element, including the basic structure and properties of the crystal lattices. The overall result is that where electrons in a magnetic domain switch from one orbital to another, there is a small change in the shape of the crystal lattice. Therefore the new orientation of the magnetic field in an individual magnetic domain causes a tendency for an extension or a contraction of the surrounding part of a sample of the material.

The behavior of the magnetostrictive materials in various applications is complex, because the changing conditions during operation causes changes in material properties. The maximum useful magnetostrictive strain is one of the key parameters defining the resulting mechanical output in the case of a magnetostrictive actuator. Magnetostriction only occurs in a material at temperatures below the Curie temperature, but when the Curie temperature is below the temperature of the environment, the magnetostriction effect has little practical value.

Magnetostrictive Cobalt Ferrite

Cobalt ferrite is a spinel and is usually assumed to have a collinear ferrimagnetic spin structure. This spinel was shown to be partially inverse with the formula $(\text{Co}_x\text{Fe}_{1-x})[\text{Co}_{1-x}\text{Fe}_{1+x}]\text{O}_4$, where the round and square brackets indicate the tetrahedral A and octahedral B sites, respectively. The ratio, Fe(A)/Fe(B), has been found to vary from 0.65 to 0.92 for quenched and slowly cooled samples, respectively. From these ratios, the distributions of the cations in tetrahedral and octahedral sites were determined to be as follows: $(\text{Co}_{0.21}\text{Fe}_{0.79})[\text{Co}_{0.79}\text{Fe}_{1.21}]\text{O}_4$ for the quenched and $(\text{Co}_{0.04}\text{Fe}_{0.96})[\text{Co}_{0.96}\text{Fe}_{1.04}]\text{O}_4$ for the slowly cooled cobalt ferrite (Sawatzky *et al.*, 1968).

Magnetic Annealing

Bozorth *et al.* (1955) measured the magnetic anisotropy and magnetostriction in various single crystals of ferrites. The effect of heat treatment with and without the presence of a strong magnetic field on the crystal anisotropy and magnetostriction was investigated. Measurements were found to be related to the initial stoichiometry and dependent on the crystal direction along which they were taken. In addition, magnetic annealing was found to have a large effect on crystal anisotropy and magnetostriction of cobalt ferrite. The magnetic anisotropy of a cobalt ferrite single crystal at room temperature was found to be as high as 4×10^6 ergs cm^{-3} . Magnetostriction is as high as 800×10^{-6} . Magnetic annealing is effective at temperatures as low as 150 °C. It causes the hysteresis loop to become square.

According to [Chen et al. \(1999\)](#), cobalt ferrite offers good mechanical properties and shows a precipitous slope of magnetostriction at low applied fields. This contributes to a high sensitivity of magnetic induction to stress, hence giving high signal-to-background noise ratios which make it suitable for sensor and actuator applications. Cobalt ferrite has been reported to show linear magnetostrictive strains up to -225×10^{-6} with a maximum strain derivative $(d\lambda/dH)_\sigma$ of $1.3 \times 10^{-9} \text{ A}^{-1} \text{ m}$ under zero applied stress. This strain derivative is an order of magnitude greater than that of Terfenol-based composites $0.2 \times 10^{-9} \text{ A}^{-1} \text{ m}$.

To further improve the magnetostrictive properties, it is essential to improve linearity of response by decreasing the magnetostrictive hysteresis and to increase the sensitivity of magnetization to stress. Magnetic annealing was found to give rise to high levels of magnetostriction and $(d\lambda/dH)_{\text{max}}$ under hard axis applied fields. A sintered sample of cobalt ferrite was annealed at 300°C in air for 36 h under a dc field of 318 kA/m (4 kOe) ([Lo et al., 2005](#)). A significant improvement in magnetostrictive properties was observed after magnetic annealing. The maximum magnetostriction increased in magnitude from -200×10^{-6} for the as-fabricated sample to -252×10^{-6} . The coercivity fields were measured to be 2.6 and 6.9 kA/m along the easy and hard axes, respectively, compared to 5.4 kA/m for the as-fabricated sample. The maximum strain derivative $(d\lambda/dH)_{\text{max}}$ in the applied field of 50 kA/m increased from 1.5×10^{-9} to $3.9 \times 10^{-9} \text{ A}^{-1} \text{ m}$.

Substituting a small amount of Mn for Fe (e.g., $\text{CoFe}_{1.8}\text{Mn}_{0.2}\text{O}_4$) increases $(d\lambda/dH)_{\text{max}}$ by 84%, substantially less than that achieved by magnetic annealing (an increase of 163%). These improved properties may degrade over time or after operation at elevated temperatures. The increase in maximum magnetostriction after magnetic annealing is attributed to the induced uniaxial anisotropy which affects domain configuration and in turn alters the measured magnetostrictive strain.

The $\langle 100 \rangle$ crystallographic directions are known to be equally easy axes of magnetization. The effect of magnetic annealing is to induce a uniaxial anisotropy superimposed onto the magnetocrystalline anisotropy, making those $\langle 100 \rangle$ directions close to the induced easy axis more energetically favorable. As a result the domains in each grain of the annealed sample tend to align along the easy directions of the grain that are close to the induced easy axis. When a magnetic field is applied along the hard axis of the annealed sample, domain magnetization re-orientations toward the field direction from local easy directions close to the induced easy axis. This results in a positive magnetostrictive strain along the easy axis but a negative strain along the hard axis.

Substitution with Foreign Ions

Substituting manganese Mn for Fe in cobalt ferrite reduced the Curie temperature linearly, by as much as 300°C in the case of $\text{CoFe}_{1.2}\text{Mn}_{0.8}\text{O}_4$. It made a modest decline in saturation magnetization (up to 20%). Maximum magnetostriction was attained with low Mn content, for example, $\text{CoFe}_{1.8}\text{Mn}_{0.2}\text{O}_4$ while it decreased with further increase in Mn content ([Paulsen et al., 2005](#)). Similar results were reported elsewhere ([Caltun et al., 2008, 2007](#)).

Magnetic anisotropy of Mn-substituted cobalt ferrites was found to increase substantially (to values that are of the order of magnitude 10^7 erg cm^{-3}) with decreasing temperature from 400 to 150°K , and to decrease with increasing Mn content. Below 150°K , it appeared that even under a maximum applied field of 5 T, the anisotropy of CoFe_2O_4 and $\text{CoFe}_{1.8}\text{Mn}_{0.2}\text{O}_4$ is so high as to prevent complete approach to saturation. Curie temperature was found to decrease linearly from 784°K for pure cobalt ferrite to 577°K for $\text{CoFe}_{1.4}\text{Mn}_{0.6}\text{O}_4$. The magnitude of the anisotropy of pure CoFe_2O_4 was found to be $2.65 \times 10^6 \text{ erg cm}^{-3}$ at 300°K ([Melikhov et al., 2006](#)). An increase in saturation magnetization for the doped cobalt ferrite was observed ([Chakrabarty et al., 2015](#)).

The stress sensitivity of Mn and Cr substituted cobalt ferrite ($\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ and $\text{CoCr}_y\text{Fe}_{2-y}\text{O}_4$) first increased as a result of Mn or Cr substitution, peaks at $x=0.2$ and $y=0.4$, and decreased below that of pure cobalt ferrite with higher Mn or Cr content. The strain derivative exhibited similar behavior as shown in [Fig. 1](#). These magnetostrictive properties were measured using the strain gage method under quasi-static applied fields up to 2 T. Mn and Cr substitutions were found to reduce both magnetostriction and anisotropy of cobalt ferrite. Moreover, within certain ranges of substitute contents anisotropy was reduced more than

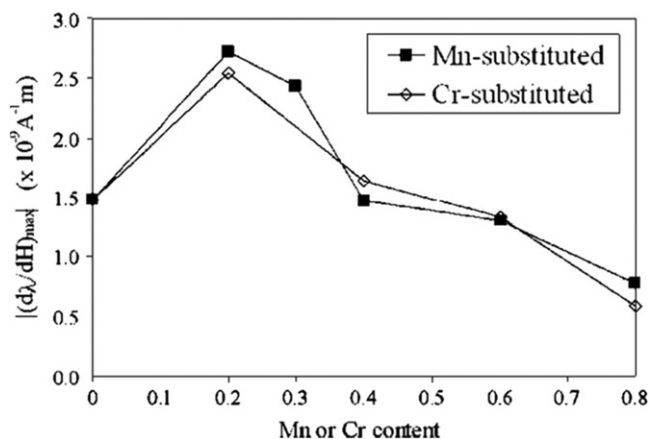


Fig. 1 The magnitude of maximum strain derivative $|(d\lambda/dH)_{\text{max}}|$ vs. the Mn or Cr content ([Lo, 2007](#)).

magnetostriction and therefore the stress sensitivity was increased as it is proportional to the ratio (λ_{max}/K) of maximum magnetostriction to cubic anisotropy constant (Lo, 2007).

The maximum magnitude of magnetostriction of Ga-substituted cobalt ferrites ($\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$) decreased monotonically with increasing gallium content over the range $x=0.0-0.8$. The rate of change of magnetostriction with applied magnetic field ($d\lambda/dH$) showed a maximum value of $3.2 \times 10^{-9} \text{ A}^{-1} \text{ m}$ for $x=0.2$ which is much higher than those of Mn- and Cr-substituted cobalt ferrites even at a much lower applied field of $H=15 \text{ kA/m}$. This enhanced $(d\lambda/dH)_{\text{max}}$ implied high stress sensitivity. Curie temperature and anisotropy energy were reduced by the substitution of Ga for Fe at a greater rate than with Mn or Cr substitutions.

The magnitude of $(d\lambda/dH)$ was expected to depend inversely on anisotropy energy (Song *et al.*, 2007).

Cobalt Ferrite Nanoparticles

Cobalt ferrite nanoparticles have recently become the subject of research interest from the point of view of the synthesis, the structure, the magnetic characterization and the application (Hou *et al.*, 2010; Kambale *et al.*, 2010; Olabi and Grunwald, 2008; Cedeño-Mattei, and Perales-Pérez, 2009; Lima *et al.*, 2015; Sattarahmady *et al.*, 2015). In addition, cobalt ferrite possesses excellent chemical stability as well as good mechanical properties. These properties could make cobalt ferrite nanoparticles a potential candidate for many biomedical applications, such as magnetic thermo-drug delivery and hyperthermia (abnormally high body temperature), magnetic resonance imaging and biosensors (Baldi *et al.*, 2007a; Amiri and Shokrollahi, 2013; Morais, 2009; Shinkai, 2002; Pita *et al.*, 2008; Matsuda *et al.*, 2015).

Kashevsky *et al.* (2008) synthesized cobalt ferrite nanoparticles using a chemical precipitation process. These particles have been studied for magnetic hyperthermia. The suspension based on cobalt ferrite nanoparticles was found not to have a toxic effect when introduced into a tumor. Kim *et al.* (2008) prepared cobalt ferrite nanoparticles which were dispersed in water, and investigated as heating agents for magnetic thermo-drug delivery and hyperthermia. The heat generation was found to be dependent on the properties of these nanoparticles, including their composition, size and crystal structure in addition to the intensity of the AC magnetic field and applied frequency. Baldi *et al.* (2007b) concluded that cobalt ferrite nanoparticles synthesized employing the successive polyol method offer the possibility to optimize the heat release capability of magnetic fluid hyperthermia (MFH) mediators at a given frequency over a wide range, just by finely tuning the particle size.

Cobalt ferrite nanoparticles were used in a core shell system in which a magnetic core of cobalt ferrite and a shell of silica are prepared via a modified Stober synthesis (Wagner *et al.*, 2002). The magnetic core was prepared by Massart's method employing cobalt and ferric chlorides. The monodisperse distribution could be obtained by means of fractionated precipitation. The average size of particles was found to be 14.5 nm. CoFe_2O_4 nanoparticles covered by a uniform silica shell have been prepared by Bonini *et al.* (2006). The nanoparticles were prepared by the co-precipitation of Co^{2+} and Fe^{3+} aqueous salt solutions by addition to a strong base solution. The sizes of the particles were in the range of 3–15 nm and their shapes were almost spherical.

However, methods for making cobalt ferrite nanoparticles are very diverse including the microwave hydrothermal flash method (Caillot *et al.*, 2004), the mechanochemical method (Shi *et al.*, 2000), the combustion methods (Kaur *et al.*, 2015; Panda *et al.*, 2015; Sundararajan *et al.*, 2015), the polymeric precursor method (Gharagozlou, 2009), the complexometric method (Thang *et al.*, 2005), microemulsions (Pillai and Shah, 1996; Calero-DdelC and Rinaldi 2007), the sol-gel technique (Avazpour *et al.*, 2015; Sajjia *et al.*, 2010), the new non-aqueous route (Ajroudi *et al.*, 2010), solvothermal method (Bi *et al.*, 2015), the forced hydrolysis method (Hanh *et al.*, 2003), the polymerized complex method (Montemayor *et al.*, 2005), and chemical co-precipitation techniques (Zare *et al.*, 2015; Reddy *et al.*, 2015). Nanoparticles prepared by these processes have different saturation magnetization and coercivity values which mainly depend on particle size. Generally, the size of these nanoparticles was found to be dependent on the heat treatment temperature. The increase in the size at higher heat treatment temperatures might be a result of the formation of crystallite clusters. Moreover, particles come into contact with each other and under favorable energetic conditions they grow (Caizer and Stefanescu, 2002).

CoFe_2O_4 nanoparticles were synthesized via the pyrolysis of polyacrylate salt precursors prepared by *in situ* polymerization of metal salts and acrylic acid (Liu *et al.*, 2005). The heat treatment at 500 °C for 3 h was considered to be moderate. The size of particles ranged from 20 to 30 nm which is a narrow size distribution. The size of particles was observed to increase up to 120 nm with increasing the heat treatment temperature up to 900 °C.

Microemulsions

Mathew and Juang (2007) described in their paper the structure of various spinel ferrites, normal and inverse. They gave a short review on the various synthesis methods of spinel ferrites in microemulsion. They found that precipitation in a water-in-oil microemulsion is a very promising technique for preparing monodisperse, ultrafine particles of controlled size and morphology. The microemulsion methods have the advantages of being economical and environmentally friendly. They involve inexpensive and less toxic iron salts in addition to the reduced amount of organic solvent.

Li *et al.* (2001) prepared cobalt ferrite nanoparticles in a size range of 10–15 nm with different $\text{Co}^{2+}/\text{Fe}^{3+}$ ratios using water-in-oil microemulsions (reverse micelles). It was found that both coercivity and blocking temperature increase with the increase of cobalt content in the ferrite structure. Similar results were observed elsewhere (Lan *et al.*, 2011) where Co-substituted ferrite nanoparticles have been prepared by the co-precipitation method. The Curie temperature T_c and saturation magnetization M_s were found to be lower than those found in larger samples, the 'bulk' properties, and to decrease with the increase of cobalt content.

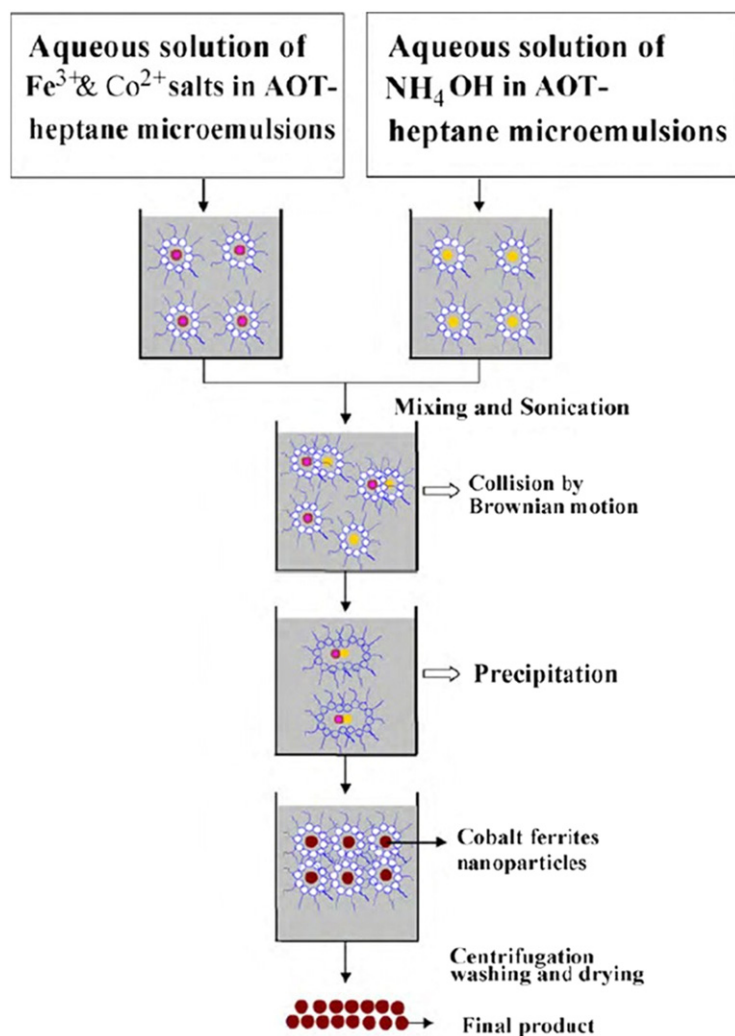


Fig. 2 A schematic representation of the synthesis of cobalt ferrite nanoparticles using the reverse micelle method (Rana *et al.*, 2010).

Cobalt ferrite nanoparticles of average size 4 nm have been synthesized by the reverse micelle approach as shown in Fig. 2 (Rana *et al.*, 2010). The preparation of nanoparticles in nano-reactors formed employing the reverse micelle technique is an attractive technique. It overcomes the difficulties associated with agglomeration and polydispersity. Three successive transformations were detected which correspond to the loss of solvent and surfactant, the onset of the amorphous to crystalline conversion and the iso-chemical transformation which is the migration of cations between octahedral and tetrahedral sites in the inverse spinel structure. These transformations were found to be irreversible.

A microemulsion is an isotropic and thermodynamically stable phase formed by at least three components; two of them are non miscible, and a third, called surfactant, has an amphiphilic behavior. When inverse micelles are used, water nano-droplets are formed in an organic compound and used as nano-reactors in order to control particle size. These nano-droplets are surrounded by a surfactant coat that limits their size and separates them from the organic compound (Pérez *et al.*, 1997).

The Co-Precipitation Method

Cobalt ferrite nanoparticles have been prepared via the co-precipitation method. Cobalt and iron nitrates were dissolved in distilled water. An aqueous solution of NaOH was used as the precipitating agent. Both solutions were added dropwise from two separate burets into a reaction vessel containing distilled water under mechanical stirring. The rate of addition was controlled in order to maintain a constant pH (8 or 10) during the process. Co-precipitation was controlled using thermostatic equipment at the desired temperature (60 or 70 °C). The precipitate was later subjected to heat treatment at 400, 500 or 600 °C for 4 h to achieve transformation into the spinel phase. The prepared particles were found to be mesoporous materials that have a particle size range of 8–45 nm with specific surface areas ranging from 99.3 to 21.4 m² g⁻¹. The particle size increased with the pH of the precipitating agent and the precipitation temperature (El-Shobaky *et al.*, 2010). Similar results were observed by El-Okr *et al.* (2011).

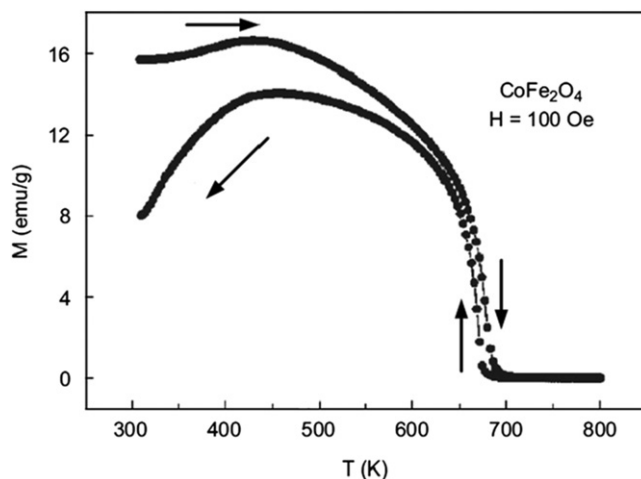


Fig. 3 Magnetization vs. temperature curve for the CoFe_2O_4 particles (Zi *et al.*, 2009).

CoFe_2O_4 nanoparticles were also prepared by the co-precipitation method using a microwave heating system in which the solution was heated to 160 °C and held at this temperature for 60 min (Bensebaa *et al.*, 2004). The crystalline structure was obtained even though the maximum temperature during preparation was 160 °C. TEM measurements indicated that the synthesized ferrite material is composed of regular nano-sized particles. According to the Scherrer Equation, the average particle size was estimated to be around 5 nm. The magnetic behavior was characterized as superparamagnetic. Magnetization measurements under magnetic field of 50 kOe (ZFC and FC) were performed. The blocking temperature was found to be around 195 °K. The AC magnetization was measured at applied field amplitude of 15 Oe and at several frequencies between 10 and 3000 Hz. The cusp, which corresponds to the transition from the blocked state to the superparamagnetic state, was found to shift to higher temperatures as the frequency of the applied AC magnetic field is increased.

CoFe_2O_4 nanoparticles have also been prepared by a modified chemical co-precipitation method. Precursors were dissolved in de-ionized water with gentle heating and then slowly poured into a well-stirred NaOH solution and left stirring for several minutes. A digestion process was performed on the mixture at 110 °C for 120 min. The gelatinous precipitate was afterwards filtered, washed several times using de-ionized water until the pH value of the solution became neutral and eventually dried at 80 °C. The as-prepared CoFe_2O_4 sample was heated from room temperature to 800 °K and then cooled to room temperature, while magnetic data was collected in a magnetic field of 100 Oe. With increasing temperature, a large drop in magnetization occurred. This was thought to be a sharp transition to the paramagnetic state. The Curie temperature T_C was found to be 677 °K when heating up and 668.6 °K when cooling down as shown in Fig. 3. This phenomenon was attributed to the change in the distribution of metal ions between the tetrahedral and the octahedral sites of the spinel structure. The increase in the degree of inversion is believed to cause the average exchange interaction to decrease, which in turn resulted in a decrease in T_C . Particles were found to be spherical and in the size range 20–30 nm. The value of saturation magnetization M_s was estimated by measurement to be 61.77 emu/g at room temperature (Zi *et al.*, 2009).

Cobalt ferrite nanoparticles have been synthesized by both a conventional and a modified co-precipitation method. The conventional coprecipitation method was modified by controlling the addition flow rate of metal ions solution to the alkaline solution under boiling conditions in order to enhance the magnetic properties of the particles by promoting their growth. The effects of the reaction time, flow rate and NaOH concentration in the process were investigated. Particles in the specific size range of 10–50 nm were observed in TEM images. The average size for particles with the highest coercivity of 4.6 kOe was estimated to be 20 nm (Cedeño-Mattei *et al.*, 2008).

Cobalt ferrite nanoparticles have also been synthesized by a process involving both spraying and co-precipitation. Particles were found to have a smaller size and to be more uniform than those prepared by the regular co-precipitation. The surface area of particles was measured by BET. The results show that the specific surface area of CoFe_2O_4 nanoparticles prepared by spraying co-precipitation, 49.8 m² g⁻¹, is much larger than the specific surface area of nanoparticles prepared by traditional co-precipitation, 17.97 g⁻¹. According to the Scherrer equation, the size of CoFe_2O_4 nanoparticles prepared by spraying co-precipitation was calculated to be 10 nm, while that of traditional co-precipitation was calculated to be 30 nm (Jiao *et al.*, 2008).

The Sol-Gel Technique

The sol-gel technique is a versatile solution process for making advanced materials, including ceramics and organic-inorganic hybrids. In general, the sol-gel process involves the transition of a solution system from a liquid 'sol' (mostly colloidal) into a solid 'gel' phase. Utilizing the sol-gel process, it is possible to fabricate advanced materials in a wide variety of forms: ultrafine or spherically shaped powders, thin film coatings, fibers, porous or dense materials, and extremely porous aerogel materials.



Fig. 4 Cobalt ferrite xerogel prepared by the sol-gel technique.

The sol-gel process, known as inorganic polymerization, was discovered in 1846 by Ebelmann (Lerouge *et al.*, 2006). In practice, the sol-gel process is very simple at the macroscopic scale. It transforms a molecule into a material ready for shaping in one step. At the nanoscopic and microscopic scales, it is in fact a very complex process involving several transformations of very different natures of matter.

The sol-gel process involves hydrolysis and condensation reactions of metal precursors (salts or alkoxides) leading to the formation of a three-dimensional inorganic network. Metal hydroxyl groups (M-OH) are formed during the hydrolysis. These groups subsequently condense into strong, rigid and irreversible metal-oxo-metal bridges (M-O-M) (Corriu and Anh, 2009; Brinker and Scherer, 1990).

A dried gel called xerogel is formed during drying by evaporation under normal conditions. Most gels are amorphous, even after drying, but many crystallize when heat treated. The final heat treatment pyrolyzes the remaining organic or inorganic components and forms the crystalline powder. This, of course, is especially useful if the gel only contains the substance which one is attempting to prepare and substances that can be removed by oxidation or evaporation. If it contains other substances, these must be removed by washing before the evaporation.

Cobalt ferrite xerogel is a dry solid containing the cobalt ferrite in an amorphous form as shown in Fig. 4. The structure still contains the remains of the original linkages of the polymer chains or skeleton, and these linkages might be arranged randomly in all directions. Heating the xerogel gives to the components, particularly the cobalt and ferric ions the possibility of migrating to sites to reduce the internal energy of the solid. Therefore on heating ions will migrate to the most favorable sites, forming close packed structures with the maximum neutralization of electrostatic charges, regardless of the original structure of the polymer. This is why crystals of cobalt ferrite grow. However by controlling the amount of heating, the rate of this process can be controlled and stopped when the crystals are still very small.

Among the various liquid-phase chemical techniques, reported in the literature and employed for the synthesis of cobalt ferrite nanoparticles, the sol-gel process (including a heat treatment operation) is probably the most effective being a feasible route to achieve high purity and homogeneity and develop crystalline nanoparticles (Sajjia *et al.*, 2012). This process offers the possibility of a generalized approach to the production of both single and complex oxide nanoparticles (O'Brien *et al.*, 2001).

Nanoparticles of cobalt ferrite having an average particle size of 40 nm were synthesized employing the sol-gel method (Gopalan *et al.*, 2009). Cobalt and ferric nitrates were used as precursors with ethylene glycol as the solvent. The temperature of the sol was increased up to 60 °C to obtain a wet gel which was then dried at 90 °C. The amorphous powder was annealed at 800 °C during the heat treatment operation by which the crystalline nanoparticles were obtained. The coercivity and remnant magnetization were found to increase in value when decreasing the temperature of measurement down to 100 °K. These nanoparticles were found to be in the ferrimagnetic state at room temperature.

The sol-gel method has been employed to fabricate CoFe_2O_4 particles by Lee *et al.* to be used as high-density magnetic recording media (Lee *et al.*, 1998). The typical spinel structure was obtained when powders were annealed at or above 350 °C. The increase in the annealing temperature yielded an increased sharpness of the major peaks of XRD patterns, indicating the growth of larger particles. A decrease in the coercivity and, in contrast, an increase in the saturation magnetization was observed with the increase of annealing temperature. The magnetic behavior was found to be related to the size of crystalline particles and the temperature of measurement. Particles annealed at 350 °C were found to be in the ferrimagnetic state at room temperature with a size range between 6 and 20 nm. Some particles were in the superparamagnetic state, existing side by side with those in the ferrimagnetic state.

Cobalt ferrite nanoparticles doped with aluminum $\text{CoFe}_{2-x}\text{Al}_x\text{O}_4$ (for $x=0.00, 0.25, 0.50$) have been synthesized by the sol-gel route (Gul and Maqsood, 2008). The precursors were dissolved in de-ionized water. Citric acid was added to the prepared aqueous solution to chelate the metal ions. A solution of ammonia was added to neutralize the solution. Drying was carried out by heating at 100 °C. The powder was then annealed at 800 °C for 6 h with a heating up rate of 5 °C/min to obtain the spinel phase. The crystallite size as calculated using the Scherrer Formula was in the range 18–23 nm. It decreased with increasing concentration of Al^{3+} ions. The lattice parameter and the Curie temperature were found to decrease as well with

increasing concentration of Al^{3+} ions. The decrease in lattice parameter was thought to be due to the substitution of the smaller Al^{3+} ions (0.51 Å) in place of the larger Fe^{3+} ions (0.64 Å) in the system. The decrease of Curie temperature from 667 to 528 °K with the increase in Al^{3+} concentration was explained as a result of the modification of the A–B interaction strength due to the change of Fe^{3+} concentration between A and B sites, reducing thereby the A–B superexchange interaction. The powder was dried and heat treated afterwards at 550 °C for 8 h in a separate investigation reported elsewhere (Aghav *et al.*, 2011). The highest value of saturation magnetization and coercivity was observed for the pure cobalt ferrite and it decreased as the aluminum content increased in the structure.

Chromium substituted cobalt ferrite nanoparticles ($\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$, $0 \leq x \leq 1$) have been synthesized using the sol–gel auto combustion method (Singhal *et al.*, 2012). The precursors were dissolved separately in distilled water. The individual solutions were then mixed together and the pH value of the solution was adjusted to about 6. The solution was then slowly heated and stirred until gels were formed. The resultant powder was annealed at 400, 600 and 1000 °C for 2 h to obtain the crystalline nanoparticles. The value of saturation magnetization was found to decrease from 77 to 13 emu g^{-1} with the increase of Cr^{3+} concentration in the structure. This was believed to be due to the smaller magnetic properties of the Cr^{3+} ions substituting for the Fe^{3+} ions in the octahedral sites. This resulted in the weakening of the A–B superexchange interaction. The value of coercivity decreased with the increase in Cr^{3+} concentration. This was attributed to the decrease in the anisotropy field. The lattice parameter was found to decrease slightly with the increase of Cr^{3+} concentration because the ionic radii of the Cr^{3+} (0.63 Å) and the Fe^{3+} (0.67 Å) ions are almost the same.

Cu doped Co ferrite nanoparticles ($\text{CoFe}_{2-x}\text{Cu}_x\text{O}_4$, $0.0 \leq x \leq 0.5$) have been prepared by the sol–gel method (Hashim *et al.*, 2012). Metal nitrates were used as precursors. They were dissolved in de-ionized water and a few drops of ethyl alcohol were added. The solution was constantly stirred until the gel formation. The temperature was kept at 65 °C during stirring. The formed gel was annealed at 200 °C for 24 h to form a fluffy loose powder. The resultant powder was then heated to, and maintained at, 800 °C for 8 h to remove any organic residuals present in the material with $10^\circ\text{C min}^{-1}$ as the heating up and the cooling down rates. The lattice constant was found to increase with increasing concentration of Cu^{2+} . This was thought to be due to the difference in the ionic radii between the Cu^{2+} ions (0.70 Å) and the Fe^{3+} ions (0.67 Å). The saturation magnetization was found to decrease with Cu^{2+} doping. The reason was related to the smaller magnetic moment of Cu^{2+} ($1\mu_B$) as compared with the Fe^{3+} ions ($5\mu_B$). Dysprosium doped Co–Zn ferrites were synthesized by a sol–gel auto combustion method reported in detail elsewhere (Kulal *et al.*, 2012). The particle sizes were found to be in the range between 30 and 40 nm. The lattice constant decreased with increasing Dy concentration while the sizes of the particles increased.

The sol–gel process has been employed to prepare composite materials as well containing highly dispersed magnetic cobalt ferrite nanoparticles as core particles in a silica matrix (Sen *et al.*, 2010; Huang and Chen, 2004). The cobalt ferrite nanoparticles were observed to interact with the silica matrix through Si–O–Fe bonds according to the IR spectrum. This interaction reaches its maximum when the temperature is raised to 600 °C. Above this temperature, the interaction disappeared with the breakage of the Si–O–Fe bonds (Zhang *et al.*, 2006). Silva *et al.* have found that the size of cobalt ferrite particles formed in the silica matrix increases with an increase in the heat treatment temperature, leading to an increase in the saturation magnetization and coercivity (Silva *et al.*, 2004). Particles stopped exhibiting superparamagnetic behavior above 400 °C when the particle size reached approximately 10 nm.

CoFe_2O_4 nanoparticles embedded in an amorphous SiO_2 matrix with a size range between 3 and 15 nm have been synthesized by the sol–gel method (Vejpravová *et al.*, 2005). Coercivity was found to increase with particle size. Due to the wide size distribution of the CoFe_2O_4 particles which were annealed at 1000 °C, the simultaneous occurrence of both sextet and doublet spectra were detected at room temperature. Particles annealed at 900 °C were all superparamagnetic as indicated by Mössbauer spectroscopy. A deviation from the ideal inverse spinel structure was observed.

The Magnetic Properties

Ai and Jiang (2010) synthesized cobalt ferrite nanoparticles by a one-step sol–gel auto-combustion method. It has been shown that the coercivity initially increased and then decreased with increasing annealing temperature whereas the particle size and saturation magnetization continuously increased. Fig. 5 shows the general relation between coercivity and particle size. Also using a low-temperature auto-combustion method, cobalt ferrite nanoparticles were prepared by Xiao *et al.* (2007). The saturation magnetization M_s , the remnant magnetization M_r , and the average particle size were found to be highly dependent upon the heat treatment temperature. Magnetic cobalt ferrite nanoparticles were synthesized by Maaz *et al.* employing a wet chemical method (Maaz *et al.*, 2007). The size of these nanoparticles was found to be dependent on annealing temperature and time due to coalescence. They found that for smaller particles the saturation magnetization had a value that was significantly lower than the bulk value while the larger sized particles had values approaching those of the bulk.

The saturation magnetization M_s of powders is generally smaller than the bulk value and is found to decrease invariably when decreasing the particle size (El-Okri *et al.*, 2011; Lu *et al.*, 2007). However, when the particle size exceeds a critical diameter, multidomain particles will usually predominate. In single domain particles, where the particle size does not exceed the critical diameter, the spins of electrons near to the surfaces of the particles are disordered compared with those in the particle core. This is considered to be one of the surface effects that contributes to decrease the saturation magnetization, M_s (Kodama *et al.*, 1996; Coey, 1971). Coercivity, H_c , is found to increase with decreasing particle size until a maximum value that is reached at the critical

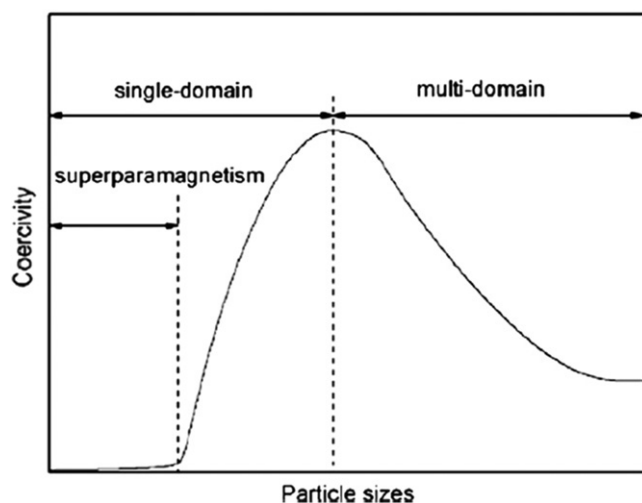


Fig. 5 The general relation between coercivity and particle size (Ai and Jiang, 2010).

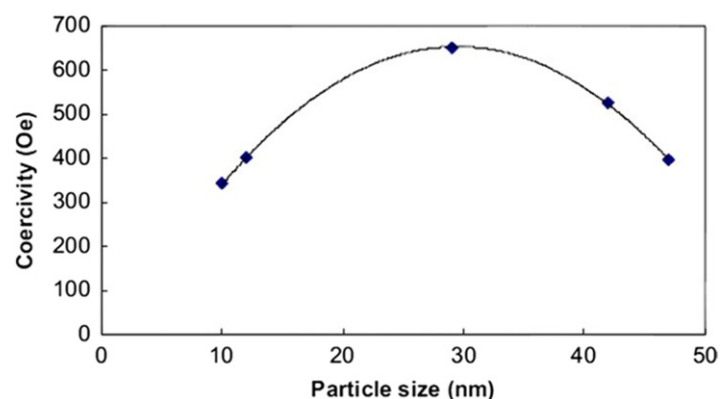


Fig. 6 The relation between coercivity and cobalt ferrite particle size (El-Okr *et al.*, 2011).

diameter corresponding to the transition stage from the multi to the single domain state. This is followed by a decrease to zero in the superparamagnetic state (Caizer and Stefanescu, 2002; Ai and Jiang, 2010; Xiao *et al.*, 2007; Zhao *et al.*, 2008). In the experimental arrangement described in Fig. 5, the coercivity of cobalt ferrite nanoparticles was found to attain a maximum value at 29 nm as shown in Fig. 6 (El-Okr *et al.*, 2011).

The magnetic properties are not only dependent on the average particle size, the size distribution and the morphology of the particles, but also on changes in the intrinsic divalent and trivalent cation distribution between the tetrahedral and octahedral sites at the nanoscale. Tahar *et al.* (2007) prepared Sm- and Gd-substituted CoFe_2O_4 nanoparticles using forced hydrolysis in polyol. The main magnetic characteristics appeared to be directly dependent on Sm^{3+} or Gd^{3+} content. A significant increase in the saturation magnetization was achieved by doping with these magnetic ions. The magnetic properties appear to be sensitive to the cation distribution between the octahedral and tetrahedral sites.

Gul *et al.* (2007) synthesized ferrite nanoparticles of $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$, with x varying from 0.0 to 0.5, by the co-precipitation method. The particle sizes were in the range of 14–21 nm. The Curie temperature was found to increase with Ni concentration in the structure. Both coercivity and saturation magnetization were found to decrease linearly with increasing Ni-concentration in cobalt ferrite (Kumar *et al.*, 2015). The decrease in coercivity was attributed to the lower magnetocrystalline anisotropy of Ni^{2+} as compared to that of Co^{2+} ions. The decreasing trend in magnetization with increasing Ni-concentration was attributed to the smaller magnetic moment of Ni^{2+} ($2\mu_B$) at the octahedral sites as compared to the Co^{2+} ($3\mu_B$). The blocking temperature as determined from the zero field cooled (ZFC) magnetization curve showed a decreasing trend with increasing Ni-concentration in cobalt ferrite nanoparticles. It was believed to be related to the magnetocrystalline anisotropy of ferrites (Maaz *et al.*, 2009).

Cobalt ferrite nanoparticles doped with Mn^{2+} have been synthesized by a polyethylene glycol-assisted hydrothermal method (Köseoglu *et al.* 2012a). PEG-400 was used as a surfactant to prevent agglomeration. The blocking temperature, coercive field and remnant magnetization were found to decrease with the increase in Mn content in the structure, while the saturation magnetization

was found to increase. Chromium doped cobalt ferrite nanoparticles have also been synthesized by polyethylene glycol (PEG) assisted hydrothermal route (Köseoglu *et al.* 2012b). Since Cr^{3+} ($3\mu_B$) has a weaker magnetic moment than Fe^{3+} ($5\mu_B$), the partial replacement of Fe^{3+} by Cr^{3+} ion caused a decrease in the saturation magnetization and coercivity in addition to a slight reduction in particle size. The addition of chromium reduced the M_s by 14% and the coercive field by 23%. Super- paramagnetic nanoparticles of Cr-substituted cobalt–zinc ferrite ($\text{Cr}_x\text{Co}_{0.5-x}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) with particle size ≈ 10 nm have been synthesized by a co-precipitation method (Sharma *et al.*, 2005). The particle size, as well as the blocking temperature, decreased with increasing Cr concentration.

Cojocariu *et al.* (2012) prepared Cr- and Mn-substituted CoFe_2O_4 ($\text{CoCr}_{0.2}\text{Fe}_{1.8}\text{O}_4$ and $\text{CoMn}_{0.2}\text{Fe}_{1.8}\text{O}_4$) nanoparticles employing the co-precipitation method. Chlorides were used as precursors. They were dissolved in distilled water and heated to 60 °C. Aqueous NaOH was added to the solutions to precipitate the powders. The precipitate was washed with distilled water, filtered, dried at 70 °C for 12 h in air and finally heat treated in three steps at 400, 650 and 900 °C for 5 h. A small increase in each of the saturation magnetization, coercivity and remnant magnetization was observed in the doped ferrites in comparison with the undoped cobalt ferrite. From the spectroscopic measurements, it was found that Co^{2+} , Mn^{3+} , Cr^{3+} ions have strong site preference for octahedral sites. The small increase of saturation magnetization was related to the oxidation state of the manganese ions as the Mn^{2+} have no particular preference for octahedral or tetrahedral sites.

Zn-substituted cobalt ferrite nanoparticles ($\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$) of a monodisperse distribution were for the first time successfully prepared via the forced hydrolysis method by (Duong *et al.*, 2007). Nanoparticles with an average size of 3 nm were in the superparamagnetic state at room temperature. The blocking temperature, T_B , decreased from 221 to 142 °K with increasing Zn substitution from $x=0$ to $x=0.4$. The saturation magnetization was found to increase with the increase of Zn content in the ferrite structure. This was due to the Zn^{2+} ions with zero magnetic moment replacing ions on the tetrahedral A-sites resulting in the increase of the total magnetic moment. The determined M_s value of CoFe_2O_4 was found to be a small amount higher than values previously reported, even with larger particle sizes. This indicated that the nanoparticles prepared by the forced hydrolysis route have a higher crystallinity than those prepared by other methods.

Cobalt ferrite nanoparticles have also been synthesized by the emulsion method (Zhao *et al.*, 2006). According to the DTA/TG analyses, the pure material was present at or above 600 °C. The particle size was observed to increase with increasing Nd^{3+} content between 400 and 500 °C, while it decreased with increasing Nd^{3+} content between 600 and 800 °C. The substitution of Fe^{3+} ions by Nd^{3+} ions resulted in the decrease of saturation magnetization from 53.4 emu/g, for the pure cobalt ferrite, to 28 emu/g, for ($\text{CoFe}_{1.8}\text{Nd}_{0.2}\text{O}_4$) and the increase of coercivity from 172 to 489 Oe. Substituting a small quantity of Fe^{3+} ions on B sites by the Nd^{3+} ions was believed to cause the superexchange interactions in the spinel structure to decrease. This resulted in a decrease of the saturation magnetization. The movement of domain walls was thought to be more difficult, due to the Nd^{3+} (content residing at) concentration increasing near grain boundaries, so that the coercivity increased.

The Effect of Surface Layer on Magnetic Properties

Toksha *et al.* (2008) synthesized cobalt ferrite nanoparticles by a method involving both sol–gel and auto combustion with a size range between 11 and 40 nm depending on the heat treatment temperature and time. The saturation magnetization M_s measured at room temperature was found to decrease with decreasing particle size. This was thought to be related to the effects of a relatively non-reactive surface layer that has lower magnetic properties. The effect of this surface layer on the magnetic properties of the whole particle increases when the particle size is very small. This leads to a decrease in the total magnetization. For particles with 15 nm as the average size and with maximum applied magnetic field of 12 kOe, the coercivity in the hysteresis loop was measured at different temperatures. The coercivity measured at room temperature (1215 Oe) was lower than the value measured at 77 °K (10.2 kOe). It is thought that this was due to significant growth in the magnetic anisotropy at 77 °K preventing the alignment of the moments under the applied magnetic field.

A random canting of the particles' surface spins caused by competing antiferromagnetic exchange interactions at the surface was proposed and explained by Coey (1971). Mössbauer-effect measurements on extremely small (6 nm) crystallites of $\gamma\text{-Fe}_2\text{O}_3$ showed that the spin configuration differs from the type found in large crystallites. It was proposed that the ions in the surface layer are inclined at various angles to the direction of the net moment. The ultrafine particles could be visualized as having a core with the normal spin arrangement and a surface layer in which the spins of the ions are inclined at some angle to their normal direction, which depends on their magnetic nearest neighbors. Parker *et al.* (1993) reported data demonstrating that the observed canting in $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (25–100 nm) is not a surface effect, but a finite-size effect. The surface spins still exhibit a weaker exchange than is found in the core states. Polarized neutron powder diffraction data of finely divided CoFe_2O_4 particles coated with oleic acid and uncoated were analyzed by Lin *et al.* (1995). They confirmed the existence of a magnetically disordered surface layer in both coated and uncoated particles. These layers are approximately 16.9 Å thick in the uncoated particles and approximately 12 Å thick in the coated particles.

Martínez *et al.* (1998) demonstrated the existence of a spin-glass-like surface layer that undergoes a magnetic transition to a frozen state below 42 °K in $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles (9–10 nm). The core of the particle was found to be ferrimagnetic that changes its orientation by coherent rotation. The spin-glass-like surface layer slowly relaxes in the direction of the field. The origin of this spin-glass-like phase at the surface could be the existence of broken bonds and translational symmetry breaking of the lattice, generating randomness in the exchange interactions that extends to some atomic layers from the surface. The thickness of spin-glass-like surface layer is evaluated to be around 6 Å by using the random-field model of exchange anisotropy. The low

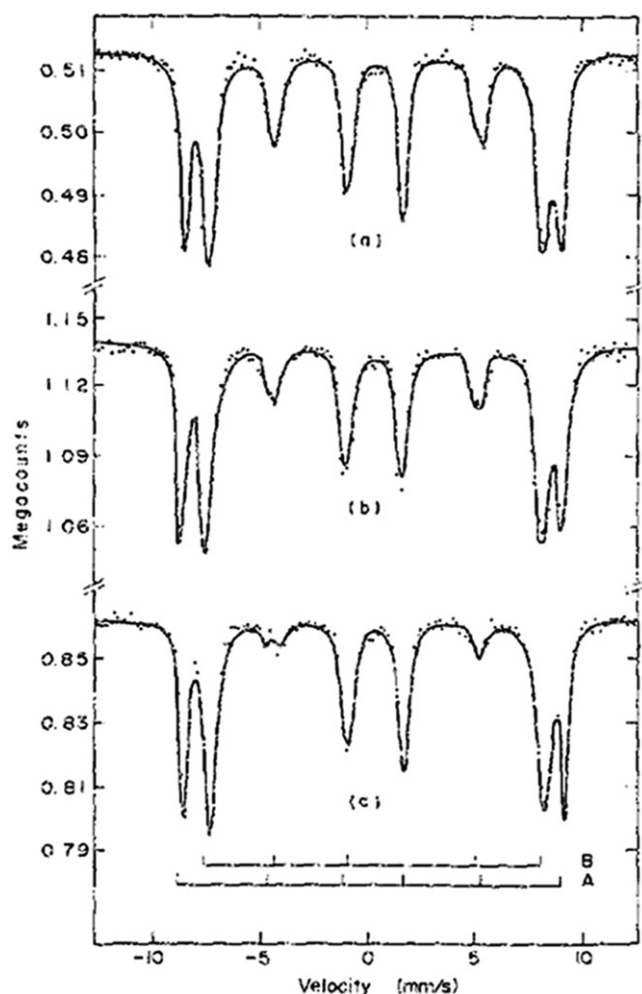


Fig. 7 Mössbauer spectra of small CoFe_2O_4 particles taken at 4.2 °K in a longitudinal external magnetic field of 50 kOe for three different samples (Haneda and Morrish, 1988).

temperature increase of H_c was observed and it is due to the pinning effect of the frozen spin-glass-like surface layer upon the single domain core.

High field irreversibility in the moment versus field and moment versus temperature of coated NiFe_2O_4 nanoparticles with average size as determined from x-ray diffraction data (65 Å) was observed. The onset temperature of this irreversibility is near 50 °K. It was proposed that the canted spins are on the particle surfaces. They freeze and form a spin-glass-like phase at temperatures below 50 °K. The surface spins have multiple stable configurations for any orientation of the core magnetization, one of which is selected by field cooling (Kodama *et al.*, 1996).

Mössbauer studies of small CoFe_2O_4 particles revealed that a non-collinear spin arrangement exists, possibly at or near the surface of CoFe_2O_4 particles (Haneda and Morrish, 1988). The particle morphology is an important factor influencing the non-collinear magnetic structure in fine particles. Mössbauer spectra at 4.2 °K were taken. Two overlapping six-line hyperfine patterns corresponding to the ^{57}Fe in B and A sites have been fitted. Mössbauer spectra were also taken with a large magnetic field 50 kOe applied along the propagation direction of the γ rays at 4.2 °K. The atomic moments lie along the direction of the external magnetic field, and the polarization conditions require the disappearance of the second and fifth lines in the hyperfine pattern. The Fe spins in small CoFe_2O_4 particles are canted with respect to the direction of the external magnetic field since substantial second and fifth absorption lines are obviously present as shown in Fig. 7. This trend increases in smaller particles and is less pronounced in larger particles. From the value of the relative intensity of the 2,5 line areas compared to the 1,6 line areas, the thickness of the spin-canted surface layer of each crystallite was evaluated.

The Net Magnetization

Cobalt ferrite particles were prepared by co-precipitation of iron and cobalt hydroxide. The precipitate was washed thoroughly, fired in a furnace at 1200 °C for 48 h and slowly cooled down to room temperature. The quenched material was obtained by

quenching the powder at 1200 °C in water. A calculation of the magnetic moments, assuming that all the Fe^{3+} ions have a moment of $5\mu_B$ and the Co^{2+} ions have a moment of $3\mu_B$, gives $3.16\mu_B$ and $3.84\mu_B$ per unit chemical formula for the slowly cooled and the quenched material, respectively (Sawatzky *et al.*, 1968). Mössbauer spectra of CoFe_2O_4 showed that this spinel is not completely inverse and that the degree of inversion depends on the heat treatment of the material. The magnetic moments of the slowly cooled and the quenched material were 3.4 and $3.9\mu_B$ per unit chemical formula, respectively, in reasonable agreement with the calculated values.

Concas *et al.* (2009) reported that the inversion degree of CoFe_2O_4 prepared via the sol-gel process may be evaluated using saturation magnetization at 4.2 °K and Mössbauer spectrum. The particle size and the thermal history are responsible for the inversion degree attained with respect to both the maximum temperature of heat treatment and the cooling rate.

The net magnetization of a ferrimagnetic material depends on cation distribution between the octahedral and tetrahedral sublattice sites. Thus, the knowledge of cation distribution is important to understand the magnetic properties of nanoparticles. In cobalt ferrite each tetrahedral Fe^{3+} ion is surrounded by twelve octahedral ions. The replacement of one Fe^{3+} ion by a Co^{2+} ion at a B site probably does not produce a large-enough percentage change in the total superexchange interaction to cause a considerable difference in the ionic moments at higher temperatures. On the other hand, an octahedral Fe^{3+} ion has only six tetrahedral nearest neighbors. If a tetrahedral Fe^{3+} ion is replaced by a Co^{2+} ion, the superexchange interaction will be reduced by an appreciable percentage. For instance, an Fe^{3+} (B) with (5Fe, °C o) nearest A neighbors would have a more rapid decrease of the moment than one with (6Fe) nearest A neighbors. The Mössbauer spectra at higher temperatures showed broader lines whereas the broadening depends on the number of probable distributions of the iron and cobalt ions in the six nearest-neighbors A-sites. The hyperfine magnetic fields at B-site nuclei have different temperature dependences for different distributions of iron and cobalt ions in neighboring A-sites.

Superparamagnetism and Ferrimagnetism

Cobalt ferrite single domain nanoparticles are known to be either in the ferrimagnetic or superparamagnetic state (Sajjia *et al.*, 2014). In these particles, magnetization can randomly flip direction under the influence of temperature. The typical time between two flips is called the Néel relaxation time. In the absence of an external magnetic field, when the time used to measure the magnetization of the nanoparticles is much longer than the Néel relaxation time, their magnetization appears to be, on average, zero. The state of these nanoparticles appears to be superparamagnetic. Furthermore, an external magnetic field is able to magnetize the nanoparticles, similarly to a paramagnet. However, the magnetic susceptibility (the degree of magnetization of a material in response to an applied magnetic field) of these nanoparticles is much larger than that of paramagnets.

On the other hand, when the time used to measure the magnetization of the nanoparticles is much smaller than the Néel relaxation time, their magnetization will not flip during the measurement so the magnetization measured will be the net of magnetic moments carried by the nanoparticles. They are said to be in the ferrimagnetic state. A transition between superparamagnetism and ferrimagnetism occurs when the measurement time equals the Néel relaxation time.

In other words, if the measurement time is kept constant and the magnetization is seen as a function of the temperature, the temperature of the transition from superparamagnetism to ferrimagnetism is called the blocking temperature, T_B . The blocking temperature is known as the temperature at which the magnetic anisotropy energy barrier of a nano magnet is overcome by thermal activation, leading to the fluctuation of its magnetization. (A magnetically anisotropic material will align its moment with one of the easy axes. An easy axis is an energetically favorable direction of spontaneous magnetization.) According to the Néel theory (Tahar *et al.*, 2007) the blocking temperature is expected to increase with K_1 , the magnetocrystalline anisotropy constant, and/or V , the average particle size. The spin-orbit interaction (any interaction of an electron's spin with its motion) is the primary source of the magnetocrystalline anisotropy. Spin-orbit interaction causes shifts in an electron's atomic energy levels (electrons in atoms and molecules can change energy levels by emitting or absorbing a photon whose energy must be exactly equal to the energy difference between the two levels) due to electromagnetic interaction between the electron's spin and the magnetic field generated by the electron's orbit around the nucleus. Above the blocking temperature T_B , there is neither remanence nor coercivity and therefore no hysteresis feature, in agreement with the superparamagnetic character of the particles. Below the blocking temperature T_B , CoFe_2O_4 nanoparticles exhibit ferrimagnetic behavior characterized by hysteresis loops with coercivity, remanence and a saturation magnetization.

Cobalt ferrite nanoparticles in the size range 5–7 nm for the use of magnetic fluid hyperthermia mediator were prepared by the successive polyol technique (Baldi *et al.*, 2007b). The Zero-field-cooled (ZFC) magnetization curve in the temperature range (2.5–300 °K) showed a peak which refers to the mean blocking temperature T_B of the assembly which was found to increase invariably with particle size. The coercive fields H_c recorded at 2.5 °K showed a decrease with decreasing particle size. At room temperature, there was no hysteresis feature observed which represents the nature of the superparamagnetic state. The same behavior was observed in cobalt ferrite nanoparticles with an average particle size of 3 nm (Calero-DdelC and Rinaldi 2007).

Moumen *et al.* (1995) reported the superparamagnetic behavior at room temperature for cobalt ferrite nanoparticles with 5 nm as an average particle size. A hysteresis feature was observed at a temperature of 20 °K for the same particles with a coercivity of 8.8 kOe and this value decreased to 4.8 kOe by decreasing the diameter of the particles from 5 to 2 nm. The details of the method of preparation of these nanoparticles for the magnetic fluid are reported elsewhere (Moumen and Pileni, 1996).

Cobalt and nickel ferrite nanoparticles with spherical-like morphology have been obtained by a solvothermal method with a size range between 5 and 10 nm (Yáñez-Vilar *et al.*, 2009). An alcohol is used as both a solvent and a ligand. Cobalt ferrite nanoparticles suspensions were found to be stable in hexanol for more than one week, while the corresponding suspensions in benzyl alcohol precipitated in less than one day. The particle size of cobalt ferrite was observed to increase from 7.6 to 8.9 nm with the increase of reaction time from 24 to 48 h, respectively. These nanoparticles were found to exhibit superparamagnetic behavior at room temperature. Saturation magnetization was found to increase from 50.2 to 58.4 emu g⁻¹ with an increase in particle size from 5.9 to 8.9 nm.

Mössbauer spectroscopy can record the sextet hyperfine structure if the magnetization of the nanoparticles does not flip during the measurement time which means that the relaxation time is longer than the measurement time. When the relaxation time is shorter than the measurement time, i.e. in a superparamagnetic state, only doublet spectrum is observed and this usually happens when the energy barriers in the nanoparticles are thermally overcome (Rondinone *et al.*, 2000). Li and Katal (2003) recorded Mössbauer spectra for cobalt ferrite nanoparticles. Results indicated that the intensity of the sextet pattern decreases with decreasing particle size while that of the central doublet increases. It has been shown that a stage exists in the transition from the ferrimagnetic to the superparamagnetic state when the particle size decreased from 10.5 to 6.3 nm. The hyperfine field at A and B sites was found to increase with decreasing particle size.

Cobalt ferrite nanoparticles have been synthesized in a homogeneous aqueous solution without any template and subsequent heat treatment (Kim *et al.*, 2003). The size of particles increased with the precipitation temperature. A particle size range between 2 and 15 nm was obtained when the precipitation temperature was in the range between 20 and 80 °C. The nanoparticles prepared at 20 and 40 °C were superparamagnetic at room temperature while those prepared at 60 and 80 °C were ferrimagnetic with magnetization values at 10 kOe of 36.0 and 58.3 emu g⁻¹ and coercivity values of 39 and 193 Oe, respectively. Mössbauer spectra recorded for nanoparticles prepared at 60 and 80 °C showed a complex hyperfine structure in which a quadrupole doublet is superimposed on a magnetically split sextet. These results could be explained by assuming that the samples being analyzed can exist with two components of particles, one consisting of superparamagnetic particles, and the other of ferrimagnetic particles because of their wide particle size distribution. The blocking temperature of nanoparticles prepared at 80 °C was found to be around 550 °K.

Conclusion

Cobalt ferrite has been of a great interest to researchers due to its pronounced magnetic properties. It has been used in many applications such as sensors and actuators. Cobalt ferrite nanoparticles have been prepared employing solution phase chemical methods, which are very diverse. The microemulsion method is a very promising technique for preparing monodisperse, ultrafine particles of controlled size and morphology. However, the sol-gel process is probably the most effective and feasible route to achieve high purity and homogeneity and develop crystalline nanoparticles. Most of the chemical methods to prepare cobalt ferrite nanoparticles produce amorphous powders. A heat treatment operation must be applied to the amorphous powders to obtain the crystalline nanoparticles. The size of these nanoparticles is found to be mainly dependent on the temperature and time of the heat treatment operation. The magnetic properties of cobalt ferrite have been discussed in detail. These properties are determined by their chemical composition and microstructure. The magnetic behavior of nanoparticles, between superparamagnetism and ferrimagnetism, was found to depend on the size, size distribution and the temperature at which the behavior is observed. The review presented in this paper is a fundamental reference guide to researchers in the field of magnetostriuctive materials.

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Sintering Behavior of Cobalt Ferrite Nanoparticles Prepared by the Sol–Gel Technique

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Introduction

Cobalt ferrite has recently become of interest to many researchers due to its promising magnetostrictive properties. It has been proposed as a suitable material for many potential applications in the area of sensors and actuators (Nlebedim *et al.*, 2010; Somaiah *et al.*, 2012; Caltun *et al.*, 2008). There have been many attempts to improve the magnetostrictive coefficient of cobalt ferrite (Bhame and Joy, 2007; Nlebedim *et al.*, 2013; Mohaideen and Joy 2013a). It has been shown that the magnetostrictive coefficient can be improved by doping with foreign ions (Rao *et al.*, 2013). And it can be further improved by magnetic annealing (Mohaideen and Joy, 2013b; Mohaideen and Joy, 2014).

The magnetic properties of ferrites are determined by the chemical composition and the microstructure (Igarashi and Okazaki, 1977; Kim *et al.*, 1994; Murthy, 2002; Ajroudi *et al.*, 2014; Mohamed and Yehia, 2014; Karimi *et al.*, 2014). Employing the conventional powder technique, ferrite powders are pressed into compacts and sintered. However, the main technical issue has always been to obtain bodies with high relative density (very low porosity), small average grain size, and narrow grain size distribution. Therefore and as sintering determines the microstructure of the end-product, acquiring a good knowledge of the operation is essential for the control and optimization of the magnetic properties sought in the finished product (Kulikowski and Leśniewski, 1980; Song *et al.*, 2014; An *et al.*, 2014).

It has been suggested that the rate of sintering activity can be improved by two main routes. The first is the addition of sintering additives (Mürbe and Töpfer, (2006); Zhu *et al.*, (2014); Mirzaee, (2014)). Different sintering additives have been proposed to enhance the densification behavior of Ni–Cu–Zn ferrites, for example, PbO (Jean *et al.*, 1999). Densification at low temperatures, boron oxide B₂O₃ has been used (Shen *et al.*, 2014).

The second route to improve the rate of sintering activity is the introduction of powders with nano-sized particles. It should result in higher surface energy in the pressed compact prior to sintering, and thus provide a higher driving force for densification and grain growth (Kolar, 2000; Wang *et al.*, 2014). Furthermore, the maximum densification rate occurs at lower sintering temperature with smaller particle sizes (Topuz *et al.*, 2015). Therefore smaller particle sizes achieve lower temperature sintering.

In a previous study, cobalt ferrite micro-sized powders were uniaxially pressed into disk samples by Rafferty *et al.* (2008). The green density of the disks was found to be about 56%. These disks were sintered with a single, continuous ramp rate to sintering temperature followed by a single dwell time at the sintering temperature.

A series of experimental trials were carried out by varying the sintering temperature in the range between 1200 and 1500 °C. After each trial, the density of the disks was measured. The maximum value of the density was found to be 87.51% for disks made from the powder with an average particle size of 14.17 µm and sintered at 1450 °C with a 3 h dwell time. Under the same sintering conditions, the density of the disks made from the powder with an average particle size of 5.34 µm instead of 14.17 µm was 4% greater.

Using the Pycnometer, it was possible to estimate the open (2.94%) and closed (9.95%) porosity for the cobalt ferrite disks made from the powder with an average particle size of 14.17 µm. This result may explain why the sintering operation with disks made using this powder was unable to obtain densities close to the theoretical value. Once the pores have changed from open to closed, it is not possible to reverse the change and gases or other materials remain trapped in the pores permanently. It is thought that a phenomenon may have occurred resulting in rapid grain growth around the pores, leading to pore closing and entrapment.

The aim of the experimental work reported in this paper is to study the behavior of cobalt ferrite nanoparticles during sintering. These nanoparticles were introduced as a solution to improve sintering activity and eventually increase the density of sintered compacts. This will result in the elimination of porosity and the production of samples with a density closer to the theoretical density value. Cobalt ferrite nanoparticles were prepared employing the sol–gel technique followed by a heat treatment operation. The structure and morphology of these nanoparticles were investigated. The density of the nanoparticles was measured using a Pycnometer.

It was proposed that a correlation could be investigated between the sintering temperature and the density of sintered disk samples. The density of disk samples was measured employing the geometrical method, a method using Archimedes principle and a helium Pycnometer. The difference between the various methods could be used to quantify the percentages of open and closed pores inside the sintered compacts.

Experimental Procedure

Nanoparticles Preparation

Cobalt ferrite nanoparticles were uniaxially pressed into disk samples. These nanoparticles were prepared beforehand employing the sol-gel technique, which is based on the formation of a stable and homogenous sol obtained through the hydrolysis and condensation reactions. The reactions take place between water, citric acid and a mixture of Cobalt (II) nitrate hexahydrate, $(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, Z99%, Fluka) and Iron (III) nitrate nonahydrate, $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$, Z98%, Sigma-Aldrich). The precursors were used without any further refinement with a molecular ratio of Co to Fe equal to 1:2. The amount of citric acid was stoichiometrically double with respect to the sum of the two metal ions.

The sol was then dried, placed in alumina crucibles (Almath Ltd., UK) and exposed to a heat treatment operation in a horizontal tube furnace (Carbolite, Sheffield, UK) at 275 °C for 3 h (Sajjia *et al.*, 2012) in flowing dry air to form the crystalline CoFe_2O_4 nanoparticles. This is all shown in Fig. 1.

Using a mixer and hotplate, a solution containing 3 wt% of PVA and 3 wt% of glycerin was formed by dissolving in distilled water. The cobalt ferrite nanoparticles were then blended into this solution and mixed thoroughly. The mixture was placed on evaporating dishes, dried at 105 °C and ground using a mortar and pestle.

Structure and Particles Size Analyses

Before mixing the nanoparticles with the binders, the structural characterization was carried out by (D8 ADVANCE-BRUKER) X-ray diffraction (XRD) equipment using Cu-K α radiation on a sample of powder whose morphology (homogeneity and particle size) was evaluated using Field Emission-Scanning Electron Microscope (FE-SEM).

Disk Samples Forming and Sintering

Disk samples were formed by uniaxially pressing 3.0 g of nanoparticles in a 20 μm diameter steel die. A load of 20 kg cm^{-2} , approximately equal to 20 bar, was applied for a duration of 20 s. These disk samples were then loaded on alumina tiles and sintered. A dwell time of 3 h was employed for the sintering. The heating-up rate was 10 °C min^{-1} while the initial cooling down rate was controlled at 5 °C min^{-1} . The binder burnout was carried out first, with a heating-up ramp rate of 0.2 °C min^{-1} to 550 °C. The temperature was then maintained at 550 °C for 1 h. The furnace was then cooled to room temperature (initial rate 5 °C min^{-1}).

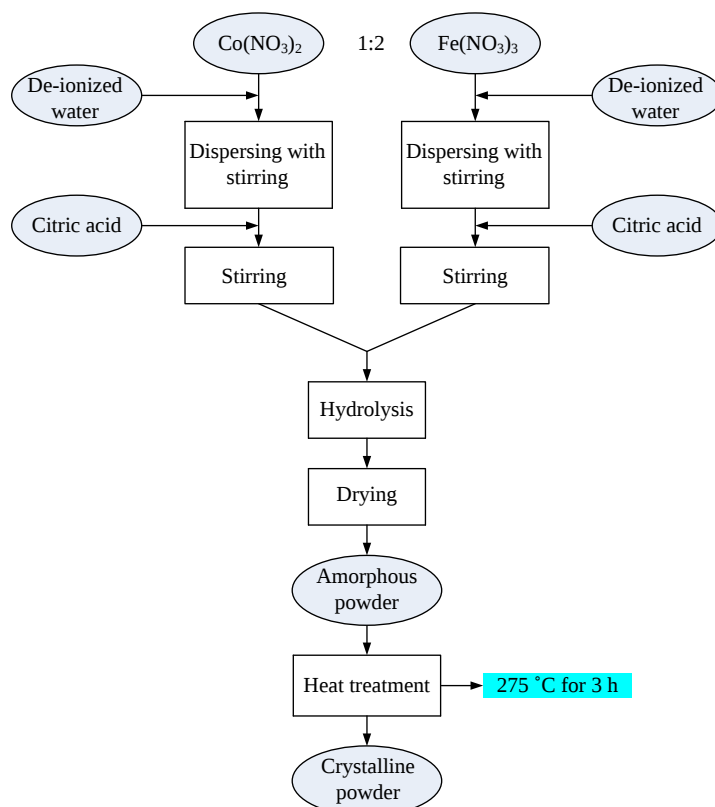


Fig. 1 Nanoparticles preparation.

Density Measurements

The density of each sintered disk sample was estimated by the geometric method. The density of these cylindrical disks was calculated using vernier calipers (with an accuracy of $0.01\ \mu\text{m}$) and a precision balance (with an accuracy of $0.0001\ \text{g}$). An average thickness was determined from the average of four diameter measurements.

A method using Archimedes' Principle was also employed to measure the density of the disk samples in addition to a helium gas Pycnometer to provide information on the closed pores. Using all these methods, it was possible to determine the percentages of open and closed porosity.

Density measurements were performed on sintered disk samples using an AccuPyc 1330 helium gas Pycnometer (Micro-meritics, USA). Initially, the sample weight was determined and then entered to the Pycnometer as an input value. The analysis measures sample volume, from which density is derived. The relative density of each sample was calculated as a percentage of bulk density to true density. True density was experimentally determined for a sample of powder using the same Pycnometer.

Results

Structure and Morphology of Nanoparticles

The preparation of cobalt ferrite nanoparticles employing the sol-gel technique has been described by (Sajjia *et al.*, 2010, 2014). The XRD pattern of the nanoparticles prepared for this study is shown in Fig. 2. All the peaks relating to the cobalt ferrite structure are visible. No additional peaks can be seen providing evidence for the formation of pure cobalt ferrite without any impurities. This pattern matches the JCPDS-ICDD file number 22-1086.

The size of particles is illustrated in Fig. 3. These nanoparticles have a size range between 5 and 25 nm (demonstrating the nano nature of resultant powder).

Sintering of Nanoparticles

A density of $5.24\ \text{g cm}^{-3}$ had been measured by Rafferty *et al.* for cobalt ferrite powder using helium gas Pycnometer (Rafferty *et al.*, 2008). This value was used as the basis for calculating the relative densities of samples in the present investigation. The cobalt ferrite nanoparticles prepared for this study were uniaxially pressed and sintered under conditions involving a single continuous ramp rate and a single dwell time. The green density of the pressed disks was calculated to be $38.97 \pm 1.88\%$.

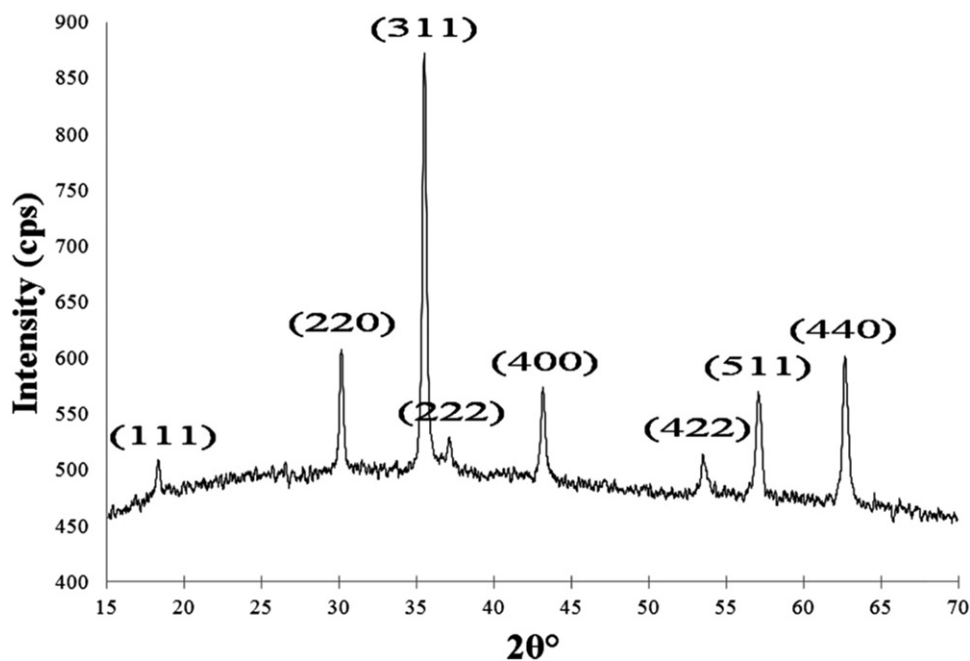


Fig. 2 XRD pattern of prepared nanoparticles.

A series of sintering trials were conducted on these disks. The sintering temperature was varied for each member of the series from 1200 to 1500 °C with intervals of 50 °C. For each set of conditions, three disk samples were sintered for corresponding measurements to estimate the density. Details of the different sintering conditions with the final densities of the samples are presented in Table 1. Each density value presented in this table, for the disk samples, is the arithmetic mean of three measurements including standard deviation.

The density is found to increase with sintering temperature up to 1350 °C. When the sintering temperature is further increased, the density decreases, as shown in Fig. 4. Peak density (with Archimedes method) $96.16 \pm 0.20\%$ was reached at the sintering temperature 1350 °C. The Pycnometer data yielded a value of $96.62 \pm 0.48\%$ at the same sintering temperature.

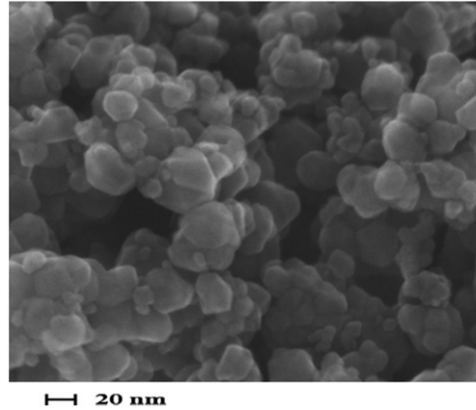


Fig. 3 Particle size and its distribution.

Table 1 Sintered disks with respective conditions and density

Sample	Temperature [°C]	Geometrical density [%]	Archimedes density [%]	Pycnometer density [%]
1	1200	94.36 ± 0.17	94.90 ± 0.10	95.43 ± 0.28
2	1250	94.91 ± 0.18	95.25 ± 0.15	95.59 ± 0.37
3	1300	95.24 ± 0.21	95.67 ± 0.20	96.10 ± 0.50
4	1350	95.71 ± 0.25	96.16 ± 0.20	96.62 ± 0.48
5	1400	94.27 ± 0.52	95.13 ± 0.17	96.00 ± 0.96
6	1450	94.01 ± 0.22	95.00 ± 0.15	95.99 ± 1.12
7	1500	93.19 ± 0.50	93.97 ± 0.23	94.75 ± 1.52

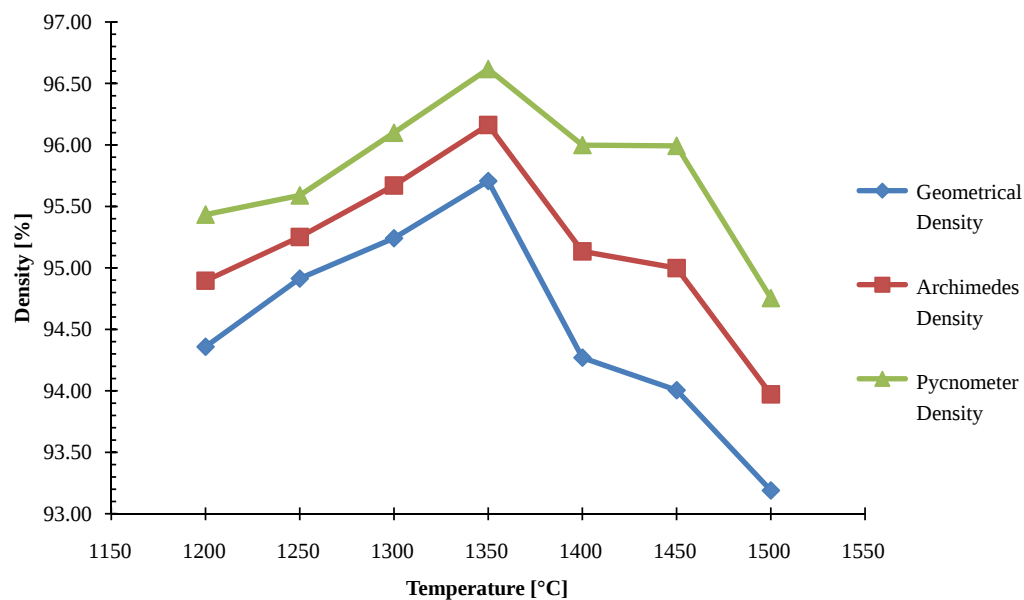


Fig. 4 Densities as function of temperature.

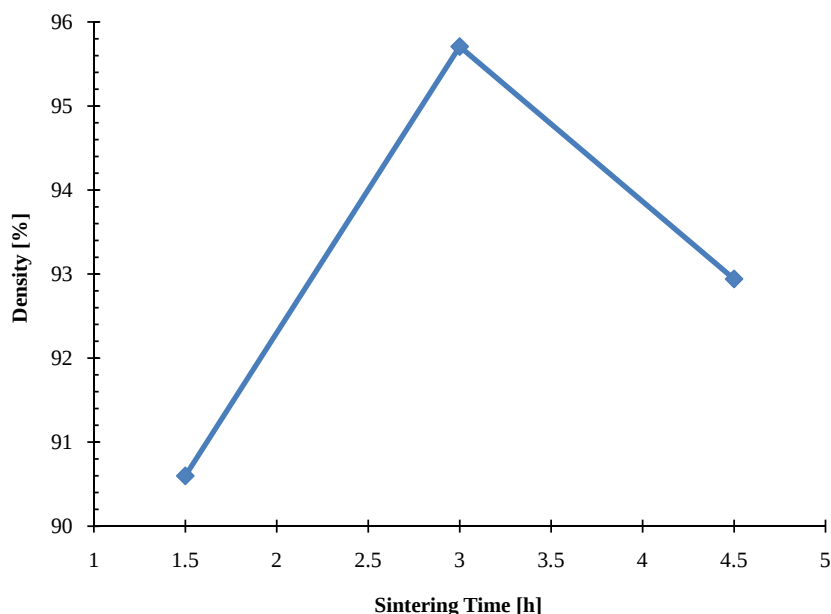


Fig. 5 Density at 1350 °C as a function of sintering time.

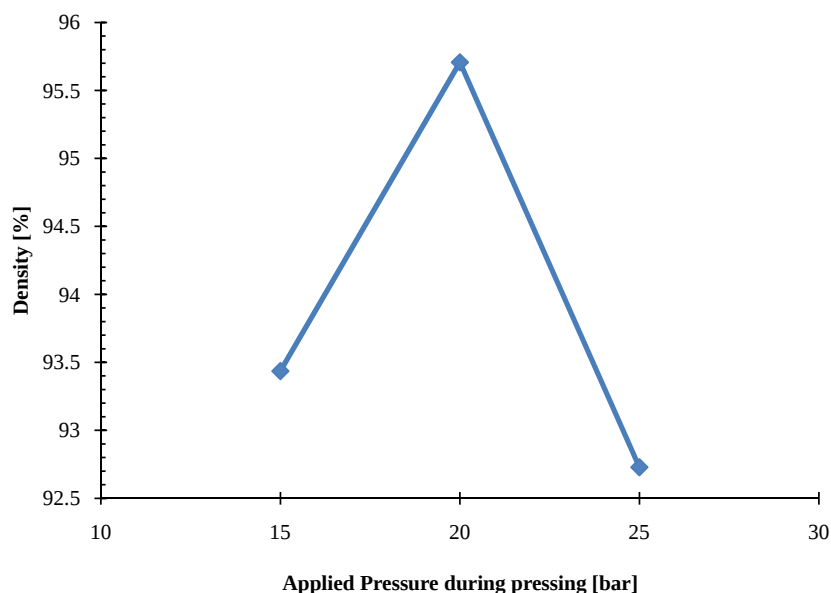


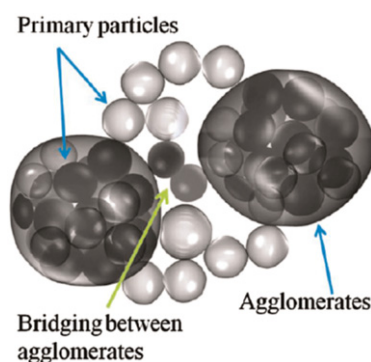
Fig. 6 Density at 1350 °C as a function of the applied pressure during pressing.

A 3 hour dwell time was found to optimize sample density after sintering at 1350 °C as shown in Fig. 5. A small number of disk samples were prepared using different applied pressures during pressing. These different pressures were 15 kg cm⁻² (lower than usual pressure in study) and 25 kg cm⁻² (higher than usual pressure in study). However, no increase in the final density was observed after making these changes in the applied pressure used when pressing, as shown in Fig. 6.

The percentages of the open and closed porosities of the prepared disk samples are shown in Table 2. The data suggest that there were a small percentage of closed pores remaining in the disk samples after sintering. The amount of closed porosity seems to have decreased at first as the sintering temperature increased. It reached a minimum at 1350 °C and then increased again as the sintering temperature was further increased. In contrast with these observations, the percentage of open porosity was found to be very small, especially when sintering at 1350 °C. This provides evidence that the sintering operation was successful in reducing some of the open porosity in these disk samples.

Table 2 Open and closed porosity

Sample	Temperature [°C]	Open porosity [%]	Closed porosity [%]
1	1200	1.07	4.57
2	1250	0.68	4.41
3	1300	0.86	3.90
4	1350	0.91	3.38
5	1400	1.73	4.00
6	1450	1.99	4.01
7	1500	1.56	5.25

**Fig. 7** Schematic of WC microstructure during the initial stage of sintering [Kumar, A., Watabe, M., and Kurokawa, K. (2011)].

Discussion

The stages of sintering are often placed into four different categories according to the observed microstructural changes. These stages are (1) from contacting particles to neck growth, (2) pore coalescence, (3) pore shrinkage, and (4) grain growth. During each stage, the microstructural features change progressively in terms of neck size, pore size and grain size. During the sintering process, both neck growth and pore shrinkage may reduce the distance between particles, and increase the sample density and shrinkage (Köferstein *et al.*, 2014).

Agglomeration by definition occurs when small particles combine to form a group and particle surfaces form a permanent or semi-permanent bonded structure. During the initial stage of sintering, the small particle groups with grain boundaries coalesce to form larger aggregates with pore boundaries as shown in Fig. 7. This results in a non-uniform microstructure and may lead to non-uniform densification during sintering. Hence, the concept of the fastest diffusion route during sintering becomes complicated as intra-agglomerate pores may densify by grain boundary diffusion while larger pores may require higher energies for densification. The mechanism seems to be strongly controlled by surface diffusion at low temperatures leading to neck growth and grain rotation. At higher temperatures, rapid grain boundary diffusion by overheating along inter-particle boundaries may be a governing sintering mechanism (Wang *et al.*, 2014; Kumar *et al.* 2011).

The mass transport mechanism was proposed to be grain boundary diffusion during the initial stage of densification in the case of nano-crystalline In_2O_3 (Sunde *et al.*, 2013). In order for this mechanism to be active, grain boundaries must have been formed by necking during heating. Therefore, it cannot be true that grain boundary diffusion is the first transport mechanism. It is common for many ceramic systems to go through regimes where surface diffusion is the most important transport mechanism in the initial stages. This leads to the formation of grain boundaries, and then grain boundary diffusion becomes the most important transport mechanism as the temperature rises. Both mechanisms cause densification but the latter mechanism also causes grain growth (McColm and Clark, 1988; Djohari and Derby, 2009; Borodianska *et al.*, 2012; Gubernat and Zych, 2014).

Effects of Sintering Temperature and Time on Density

As it has been observed, the density of disk samples increased as the temperature increased from 1200 to 1350 °C. The density reached a maximum value at 1350 °C and decreased as the temperature was increased further toward 1500 °C. These changes could be due to the following factors. First, a significant amount of grain growth accompanied by pore entrapment is believed to happen at higher sintering temperatures (Liu *et al.*, 2014). On the other hand, grain boundary diffusion as discussed above is believed to be relatively small at lower sintering temperatures. Therefore, this mechanism did not contribute to the densification activity to the same extent at lower temperatures. This caused the densification rate to be smaller at lower temperatures and as a consequence, the disks remained more porous.

The results obtained when the dwell time was shortened to less than the 3 h are relatively easy to explain. Clearly a shorter dwell time was not long enough for the sintering to be completed, and, as a result, the porosity was not eliminated. This reasoning can be concluded because, when the dwell time was extended to 3 h, the final density of the disks increased and therefore, more porosity was eliminated during the sintering.

However, the results for more than 3 h dwell time are more difficult to explain. The longer dwell times also had a negative effect on the sintering and may have caused a de-sintering process to take place. As pores can become smaller during the different stages of sintering, they can also become larger (e.g., link together). Increased pore size can be due to several causes such as the disappearance of the neck and grain boundary between two grains. This phenomenon is described as de-sintering. It is generally, but not exclusively, associated with grain growth. De-sintering caused the pores to increase in size and become trapped (Lange, 1996).

Effects of Applied Pressure During Pressing Stage on Density

It is likely that applying a lower pressure during pressing may result in unusually weak disks. The pressure was required to bring the nanoparticles sufficiently close to each other so that the organic binders on their surfaces could act as glues, holding the particles together, and preserving the shape of the disk. However, most deformation of the compact may have occurred in response to the applied pressure, causing particles to move relative to one another, and reduce the pore volume in the compact.

Also, there would have been a tendency for the stresses produced by the hydraulic equipment to be magnified at certain points because the particles were not totally spherical in shape. On some occasions, this magnification may have resulted in developing fractures in the particles. This would happen more regularly if the particles had sharp points or jagged edges. Because of this characteristic, there would have also been a reduction in the volume of the compact and the porosity would have been also reduced.

On a smaller scale, there would have also been a deformation of the organic binder layers existing as a coating on each nanoparticle surface. Therefore, the decrease in the pore volume in the compact from increased pressure might be significant. For the same reasons, if the pressure applied during disk production was unusually low, the effect on the porosity would also be significant. Therefore, it is true that the porosity in the compact would be greater if the applied pressure was smaller.

The above explanation, for the existence of variations in porosity in the compacts before sintering, would be generally accepted by other investigators (Xu *et al.*, 2014). However, the following results of experimental trials reported in this investigation would not have been anticipated. The variation of porosity magnitude from different pressures during disk production has apparent impact on sample density variation, even after the sintering operation.

Employing a higher value of applied pressure for the pressing of the disks also resulted in a reduction of the density of the samples in measurements carried out after the sintering operation. It is especially difficult to explain this second effect, namely, an above average density before sintering to a below average density after the treatment. Increased pressure in the die would have created more cracks (micro) in the compact in its green state, but these cracks would occur in individual particles of the microstructure as described above. This would have produced less porosity and a greater packing density of the particles. Both of these features would be expected to facilitate the subsequent sintering operation, even though it also resulted in slightly more particles in the compact. It is expected that the sintering operation would result in improved properties.

However, increased pressure in the die during the pressing stage may have created more cracks on a larger scale (macro) in the compact (green state) after pressing during disk sample extractions from the die. Some of these cracks may have maintained some of their existence during and after sintering. These cracks were thought to be the main reason behind the resultant lower density.

Density of Cobalt Ferrite Nanoparticles

It should be noted that a test was carried out using a helium gas Pycnometer, type AccuPyc 1330 V1.02, to determine the true density of a sample of the nanoparticles. The value obtained was $4.93 \pm 0.0118 \text{ g cm}^{-3}$ which is very different from the value of 5.24 g cm^{-3} reported by (Rafferty *et al.*, 2008). Moreover, a sample of the same powder was sent outside the University laboratory for the same test to be carried out, using a different helium gas Pycnometer (type AccuPycII 1340 V1.05), and a value of $4.95 \pm 0.0029 \text{ g cm}^{-3}$ was obtained. The agreement between the two Pycnometers is impressive.

The reason for this disparity may be due to the nature of this particular sample of cobalt ferrite nanoparticles. This is because these particles are known to have been magnetically active, and there is evidence that the majority of them were small enough to have only one magnetic domain (Sajjia *et al.*, 2014). At room temperature and under atmospheric pressure, there would have been a tendency for these particles to arrange themselves as to minimize the magnetostatic energy of the whole sample of nanoparticles.

This phenomenon could be done by allowing the nanoparticles in a sample to form large rings or hoops and join each other in series around an empty space inside the ring. If such temporary structures are formed frequently enough throughout the sample, nanoparticles may occupy a volume which is larger than the one they would occupy if they were not magnetic (micro-sized particles). This may explain why some techniques designed to measure density may provide excessively low values.

However, when the helium gas Pycnometer measures density, gas may penetrate through such loose structures to the empty internal space, and provide density values that conform more to the known density of individual particles. If these ideas explain density results better, it is not known why the Pycnometer is not able to penetrate to the centers of these structures. Furthermore, when measuring the density of powder samples with larger particles, each particle would have many magnetic domains. Con-

sequently there would be no reason for the ring or hoop -like structures to form. It follows in turn that the density measuring equipment would provide the more normal and higher values.

A similar phenomenon was observed after the pressing stage. The calculated green density of $38.97 \pm 1.88\%$ reported for compacts made from cobalt ferrite nanoparticles, indicates that a similar effect may have occurred causing a decrease in the density. This value is much smaller than the average value of 56% reported for compacts made from micro-sized cobalt ferrite powder. Perhaps the two effects are related, and the disparity in density observed before powder pressing is preserved even after the pressing stage.

Conclusions

The sintering behavior of cobalt ferrite nanoparticles was investigated. Cobalt ferrite nanoparticles were successfully prepared employing the sol-gel technique. These nanoparticles were without any impurities. The particle size was found to be in the 5–25 μm range. Disk samples were prepared employing a uniaxial press using a pressure of 20 kg cm^{-2} . Sintering trails were then conducted. A maximum relative density of 96% was reached at 1350°C with a dwell time of 3 h. The density did not increase to a higher value but a number of changes were made to the period of the dwell time. Similarly no higher values of the density were obtained when the pressure used to form the disk samples was varied.

Cobalt ferrite nanoparticles were found to behave in a unique way that resulted in a decrease in their true density from 5.24 to 4.94 g cm^{-3} . This behavior was observed during the pressing stage as well. The green density forming 38% of compacts was found to be smaller than 56% reported in the literature. The maximum density obtained in this study for sintered compacts was found to be 4% higher than results found in the literature when employing micro-sized powders with a one-step sintering temperature profile.

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Nanoscale Memristor

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Glossary

R	Resistor
L	Inductor
CMOS	Complementary Metal Oxide Semiconductor
R_{int}	Internal State Resistance
ROFF	Resistance of Undoped Region
μ_n	Dopant Mobility
FEM	Finite Element Modeler
NVM	Non-volatile Memory
SiO	Silicon Oxide
STT	Spin Torque Transfer
TiO_{2-x}	Titanium Dioxide (Magneli State)
BMD	Bipolar Memristive Devices
UMD	Unipolar Memristive Devices
C	Capacitor
M	Memristor
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
R_i	Initial State of Memristor
RON	Resistance of Doped Region
ϵ	Dielectric Constant
HfO₂	Hafnium Dioxide
SrTiO₃	Strontium Titanate Trioxide
TiO₂	Titanium Dioxide
EFI	Electromagnetic Field Interpretation
BRS	Bipolar Resistive Switches
URS	Unipolar Resistive Switches

The memristor, a portmanteau of ‘memory resistor’ was a term coined by circuit theorist, [Chua \(1971\)](#), as a missing two-terminal nonlinear passive electrical component relating electric charge and magnetic flux linkage. The operation of RRAM devices was recently connected to the memristor concept ([Strukov et al., 2008](#)). Theoretical postulation of memristor is well-described in Section “Theoretical Postulation” followed by the characterization of memristor as a device model. Behavior of memristor for different input signals like sinusoidal, pulses, triangular wave, and constant DC is documented in Section “Current–Voltage (I–V) Characteristics” The variation is reported as per resistance change with time and the effect of voltage of its operation that demonstrates the memristive effect. Various types of memristors has been documented in Section “Types of Memristors” Memristor can be implemented in many applications like as from nonvolatile memory to signal processing and everything in-between, including remote sensing, high-speed computing architectures, neuromorphic and biological systems. Applications of this nanoscale device is given in Section “Applications” followed by summary.

Introduction

Information Technology systems now take up 2% of the world’s electric power. Now-a-days, We need IT systems that are 1000 times more powerful, we need what is called exascale computing: the need for a radical new type of computer architecture. Yet to get there it would take too much electric power. The memristor makes exascale possible.

Memristor¹ is basically the fourth class of basic electrical circuit element ([Chua 1971](#)), adjoining the most common resistor R, the capacitor C, and the inductor L, that exhibit their unique properties primarily at the nanoscale level. Theoretically, Memristors or the memristive systems, a short of ‘memory resistors,’ are a type of basic circuit elements that are passive and

¹The term *Memristor* and *Memristive* systems can be used interchangeably.

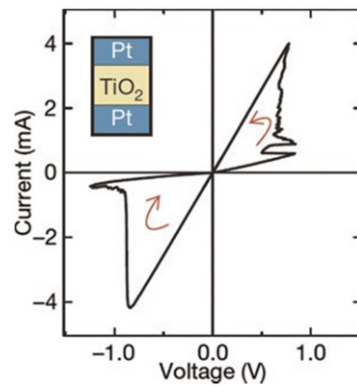


Fig. 1 Pinched hysteresis loop of Memristor. Strukov, D., Snider, G., Stewart, D., Williams, R., 2008. The missing memristor found. *Nature*. 453 (7191), 80–83, a 2008; reproduced with permission from Nature Publishing Group.

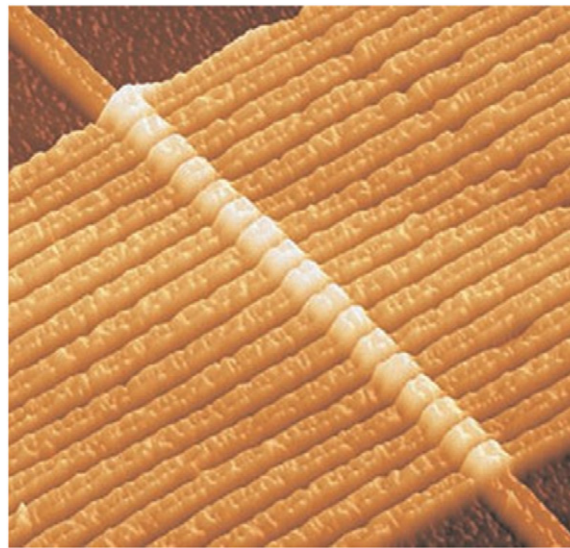


Fig. 2 Prototype of TiO_2 Memristor. Bush, S., 2008. HP nano device implements memristor. *Electronics Weekly*.

maintain a relationship between the voltage v and the time integrals of current i between a two-terminal device. Thus, a memristor's state or in simple word resistance varies as per the device's memristance function $M(q)$, allowing, through small read levels, access to a 'history' or previous state of applied current or voltage Chua (1969). The material implementation or simply the IMPLY of memristor effects can be determined by the characteristics such as hysteresis (an increasing rate of change as object change state from one to another) which, like various other nonlinear 'anomalies' in circuit theory, ought to be less anomaly than a basic property of passive circuits (Chua and Kang, 1976). Until recently, when the team at HP Labs under scientist Stanley Williams developed the first stable and practice prototype, memristance as a property of a known material was nearly nonexistent or not known as common as shown in Fig. 2 and its I - V characteristics are given in Fig. 1. The effect of memristor at non nanoscale distances is dwarfed by electronic and other field effects, until materials and scales that are in the size of nanometer are utilized (Xia *et al.*, 2009). At the nanoscale level, these properties have been observed in action before the development of HP Labs prototypes (Radwan *et al.*, 2010).

But beyond the physics of electrical and electronic engineering, they are reconceptualizing of an electronic circuit theory that is passive and first proposed in the year 1971 by the nonlinear circuit theorist, Leon O. Chua. Leon Chua, a Professor at the University of California at Berkeley, contended in his paper published in 1971 *Transactions on Circuit Theory* (Chua (1971), is that the most fundamental relation in passive circuitry was not in-between charge and voltage as assumed, but it is in between changes- in-voltage, or flux ϕ , and charge q . Chua has stated: The situation is very much analogous to 'Aristotle's Law of Motion, which was wrong, because he said that force must be proportional to velocity' (Adhikari and Kim, 2012; Adhikari *et al.*, 2013). This misled many people for almost 2000 years until Isaac Newton came along and pointed out that the Aristotle was taking wrong variables. Isaac Newton demonstrated that the force is proportional to acceleration of the change in velocity. This postulation is exactly the similar situation with electronic circuit theory exists today. Most of the electronic

textbooks have been teaching by the variables that are wrong – voltage and charge explaining away inaccuracies as anomalies. and except that they should have been teaching the fundamental relation in between changes occur in voltage v , or flux ϕ , and charge q (Shin *et al.*, 2010).

As memristors develop, it is going to come down to who can come up with the best material implementation of memristor. Currently IBM, Hewlett Packard (HP), Samsung, HRL, and many other research labs seem to be hovering around the most popular titanium dioxide (TiO₂) memristor, but there are still a few other types of memristors with vectors of inquiry.

Current generation CMOS technology puts a constraint on further improvements in the area of speed and power due to non-availability of headroom. As CMOS-based devices meet its performance limits, new methods, technologies, and materials that are required to further break into new advance computing devices. Switches like MOSFETs are extensively used as a basic building block to develop variety of digital logics and devices like memories, gates, signal processing chips, etc. Speed and compact devices are highly regarded in VLSI industry. Hence, the need of new type of devices arise. Memristors and memristive devices are the hybrid result of two extensively researched areas viz. materials and architecture. Lots of possibilities are hidden behind in these recently developed device. These are memory elements that can store data over a much larger span of time even being passive. After the postulation of this device in theory and till its prototype appearance, it took almost 35 years.

The incredible memristor can perform the following:

- Store data like DRAM or Flash but it does not require any energy to maintain the data storage.
- The memristor chips can be laid down in layer upon layer, creating three-dimensional structures that can store and process data.
- The memristor is easy to make and completely compatible with today's CMOS chip-making processes.
- It can be scaled to very small geometries without losing its properties.
- The memristor can also perform logic, it can act as a microprocessor.

Theoretical Postulation

Theory is the basis of understanding anything, so as with memristors; the theory is postulated by circuit theorist, Chua (1971), almost 40 years back and from then it took almost 35 years from theory to actual device fabrication.

Memristor – The Missing Circuit Element

Chua and Kang (1976) presented the logical and scientific basis for the existence of a new two-terminal circuit element called the memristor (a contraction for memory resistor) which has every right to be as basic as the three classical circuit elements already in existence, namely, the resistor, the inductor, and the capacitor. Although the existence of a memristor in the form of a physical device without internal power supply has not been discovered, its laboratory realization in the form of active circuits is presented in his paper published in *IEEE Transactions on Circuits Theory*, 1971. Many interesting circuit-theoretic properties possessed by the memristor, the most important of which is perhaps the passivity property which provides the circuit-theoretic basis for its physical

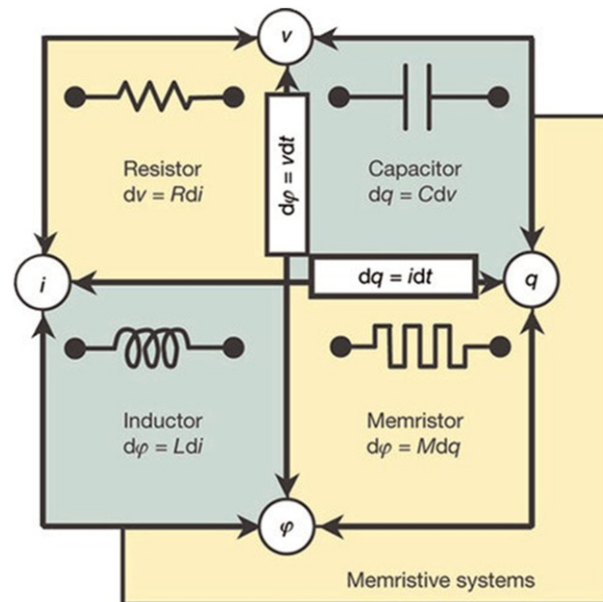


Fig. 3 The four fundamental two-terminal circuit elements: resistor R , capacitor C , inductor L , and memristor M . Strukov, D., Snider, G., Stewart, D., Williams, R., 2008. The missing memristor found. *Nature*. 453 (7191), 80–83, a 2008; reproduced with permission from Nature Publishing Group.



Fig. 4 Memristor Symbol. (Source: <http://www.memristor.org/>).

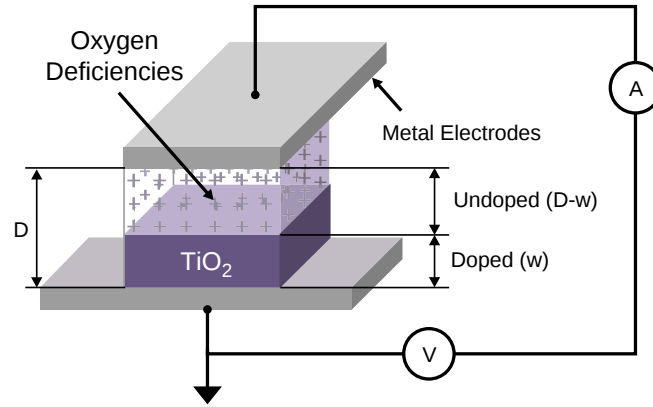


Fig. 5 Linear ion drift memristor model with two regions viz. doped w and undoped $D-w$. The electrodes are connected with voltage source.

realizability, is also derived in that paper. An electromagnetic field interpretation of the memristor characterization with the help of a quasi-static expansion of Maxwell's equations is demonstrated (Chua and Kang, 1976). Chua also proposed some novel applications of memristors in his paper. The relationship between four basic circuit elements are shown in Fig. 3 (Strukov *et al.*, 2008).

On the Symmetry Forefront

Chua postulated that from the circuit-theoretic point of view, the three basic two-terminal circuit elements are defined in terms of a relationship between two of the four fundamental circuit variables, namely; the *current* i , the *voltage* v , the *charge* q , and the *flux-linkage* ϕ . Out of the six possible combinations of these four variables, five have led to well-known relationships Chua (1969). Two of these relationships are already given by

$$q(t) = \int_{-\infty}^t i(\tau) d(\tau) \quad (1)$$

$$\phi(t) = \int_{-\infty}^t v(\tau) d(\tau) \quad (2)$$

Three other relationships are given, respectively, by the axiomatic definition of the three classical circuit elements, namely, the resistor (defined by a relationship between v and i), the inductor (defined by a relationship between ϕ and i), and the capacitor (defined by a relationship between q and v). Only one relationship remains undefined, the relationship between ϕ and q . From the logical as well as axiomatic points of view, it is necessary for the sake of completeness to postulate the existence of a fourth basic two-terminal circuit element which is characterized by a ϕ - q curve. This element will henceforth be called the *memristor* because, as will be shown later, it behaves somewhat like a non-linear resistor with memory. The proposed symbol of a memristor for relation ϕ - q is shown in Fig. 4.

Device Model

Linear ion drift memristor use a finite length two-terminal device, say the length is denoted by D for the whole region as shown in Fig. 5. There are two regions, one is doped and other is undoped region. Two metal electrodes on both sides serve the purpose of input and output signal terminals. Length D of the region consists doped region w and undoped region $D-w$. For a voltage driven memristor, voltage V is applied at one terminal. As this is a basic circuit element and that too passive, it does not need continuous power supply to remember its state.

In Linear ion drift memristor that is designed using TiO_2 , when voltage is applied across the device, ions basically the oxygen atoms from TiO_2 travels from doped region to undoped region thus completing the internal path and reduces the resistance of device Blanc and Staebler (1971). But when the voltage is removed, the oxygen atoms again attracts towards doped region thus leaving undoped region in higher resistance state. Let resistance of undoped region is R_{OFF} and resistance of doped region is R_{ON} . The equivalent circuit of linear ion drift memristor is shown in Fig. 6.

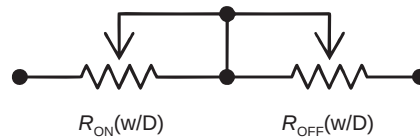


Fig. 6 Equivalent circuit of linear ion drift memristor; where R_{ON} is the variable resistance of doped region and R_{OFF} is the resistance of undoped region. These are connected in series because the two regions are combined and their equivalent resistance is calculated. Strukov, D., Snider, G., Stewart, D., Williams, R., 2008. The missing memristor found. Nature. 453 (7191), 80–83, a 2008; reproduced with permission from Nature Publishing Group.

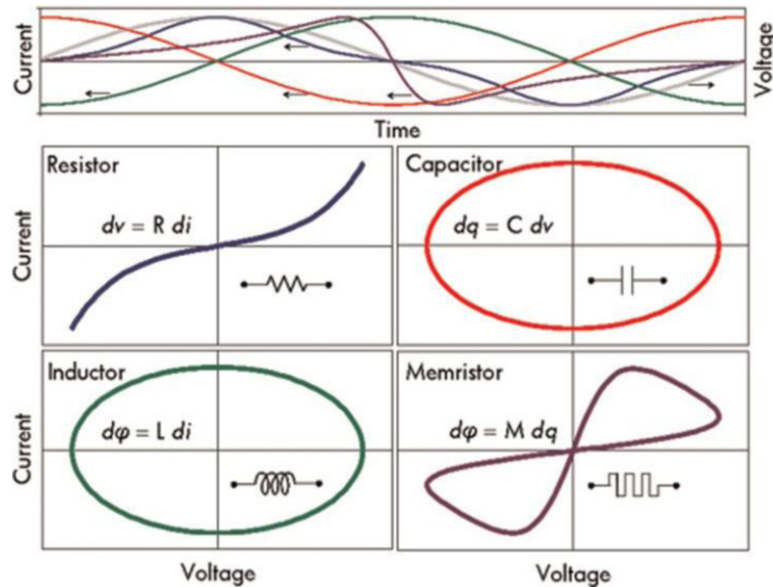


Fig. 7 Lissajous figures of resistor R , capacitor C , inductor L , and memristor M under the applied bias. Mellor C 2011 Memristor and memresistor history. The Channel (News). <http://www.channelregister.co.uk/>.

Table 1 Specifications of linear ion drift memristor model

Sr.	Parameter	Specifications
01	Device length, D	10×10^{-9} m
02	Dopant Mobility, μ_v	1×10^{-14} cm/(V s)
03	Doped Region, w	1.5×10^{-9} m
04	Initial Resistance, R_i	$1 \times 10^3 \Omega$
05	Undoped resistance, R_{OFF}	$30 \sim 50 \Omega$
06	Doped resistance, R_{ON}	100Ω
07	Doped region material	TiO ₂
08	Undoped region material	TiO ₂ — x
09	Dielectric constant, ϵ_r	115

As memristor is the known as the ‘missing’ circuit element, because it took a long time to discover. If the memristor, with memristance M , provides a relation between charge q and flux ϕ , then

$$d\phi = M dq \quad (3)$$

As per the case of linear elements, if M is a constant, the memristance is equivalent to resistance and does not having any special effect for circuits but, however, if M is the function of charge q which further yields a nonlinear element, then the situation becomes much more fascinating. The I – V characteristics of memristor for a relation between charge q and flux ϕ for a sinusoidal wave input is a frequency-dependent Lissajous figure as shown in Fig. 7 and no any passive circuit element can duplicate this properties thus making it stand out. Some typical specifications of memristor device model is shown in Table 1.

Memristor Characterization

The most basic mathematical equation of a current-controlled memristor in differential form is:

$$v = R(w)i \quad (4)$$

where, the state variable of the device is w and R is domed as the resistance that depends on the internal state of the memristor.

$$\frac{dw}{dt} = t \quad (5)$$

The unique property that separates memristor from rest of the devices and no any basic circuit element possess same properties is that; the memristor remembers the last current passed through it. For example, if we apply 1 mA current through it, it remembers the state even if we remove the potential/source across it. Whenever we'll reapply the source the resistance R of a device will be on the same value until and unless you apply higher potential to it. Then, if you increase the potential it then remembers the next state and the memory effect will retain the state and this process goes on.

The memristive systems are the concept of a broader class of nonlinear dynamical systems which is further described by the equations

$$v = R(w, i)i \quad (6)$$

$$\frac{dw}{dt} = f(w, i) \quad (7)$$

where, w is the set of state variables and R and f is the general explicit functions of time.

Electrical switching in thin-film devices is highly regarded area due to the fact that this technology can enable scaling of the logic and memory elements beyond the limits of CMOS technology (Kuekes *et al.*, 2005; Strukov and Likharev, 2007).

The external bias of voltage with respect to time $v(t)$ when applied across the device will move the internal boundary between the two regions viz. doped and undoped by causing the charged dopants to drift from positive to negative terminal (Blanc and Staebler, 1971). The ohmic conduction and linear ion drift in a uniform field of length D with an average ion mobility m_v , the voltage across it can be characterized by using

$$v(t) = \left(R_{ON} \frac{w(t)}{D} + R_{OFF} \left(1 - \frac{w(t)}{D} \right) \right) \quad (8)$$

$$\frac{dw(t)}{dt} = \mu_v \frac{R_{ON}}{D} i(t) \quad (9)$$

which further yields the following equation for $w(t)$:

$$w(t) = \mu_v \frac{R_{ON}}{D} q(t) \quad (10)$$

By plugging the eqn [10] into [8], we can obtain the memristance of system, which is further $R_{OFF} \gg R_{ON}$ reduces to:

$$M(q) = R_{OFF} \left(1 - \frac{\mu_v R_{ON}}{D^2} q(t) \right) \quad (11)$$

In eqn [11], the charge $q(t)$ is crucial to memristance and it becomes larger in value for higher dopant mobilities m_v and quite smaller for thin-film thicknesses D .

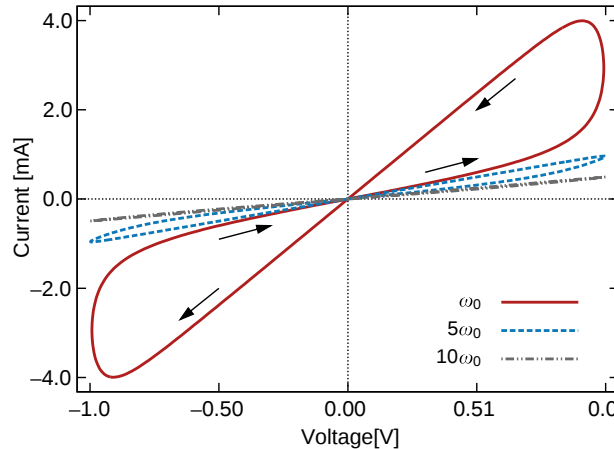


Fig. 8 Hysteresis loop of linear ion drift memristor for frequencies viz. ω_0 , $5\omega_0$, and $10\omega_0$ under the applied voltage bias of 1.0 V. The maximum current flows through the memristor is ω_0 is 4.0 mA. Singh, T., 2015. Hybrid Memristor-CMOS (MeMOS) based Logic Gates and Adder Circuit. arXiv (cs.ET) preprint arXiv:1506.06735, pp. 1–11.

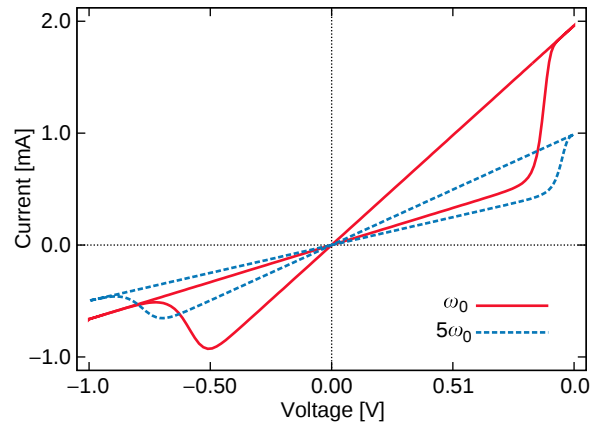


Fig. 9 Change of I - V characteristics under the influence of internal state resistance R_{int} variation. The plot is given for frequencies ω_0 and $5\omega_0$. The downward curved gets its pointed position for larger internal resistance of device. Singh, T., 2014. Design and analysis of Memristor: The missing circuit element. Master's Thesis. Disp. Electron. Elect. Eng., Lovely Professional University, PB, India.

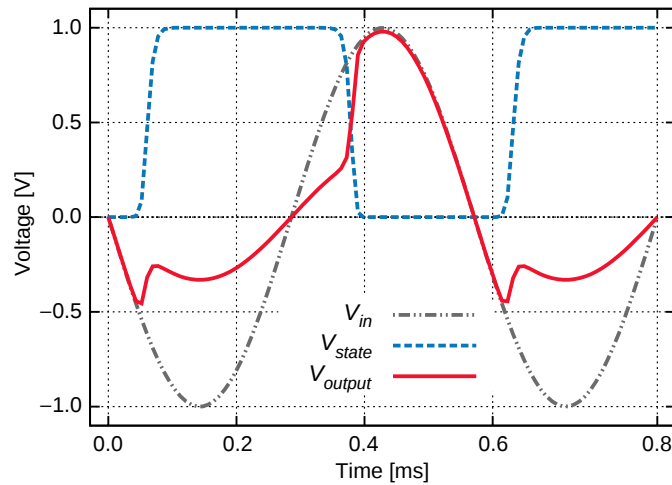


Fig. 10 Input signals plot for the I - V characteristics given in Fig. 8. Input sinusoidal signal, output voltage/input current signal, and internal state signal is represented for 1.0 V bias. Singh, T., 2014. Design and analysis of Memristor: The missing circuit element. Master's Thesis. Disp. Electron. Elect. Eng., Lovely Professional University, PB, India.

From the result, it can be stated that as the frequency increases the hysteresis curve starts shrinking towards the origin but the slant of curve remains same, more specifically as the frequency increases the current passing through the memristor decreases. It starts operating in milliamperes to microampere range. At higher frequencies, the variation in between resistance starts reducing. From Fig. 8, it can be concluded that at frequency ω_0 , the maximum current sweeps from -4.0 to 4.0 mA. At frequency $5\omega_0$, the current sweep reduces to 1.0 mA range and if the frequency is further doubled, i.e., at $10\omega_0$ the maximum current sweeps in 0.5 mA region.

Effect of Internal Resistance State, R_{int}

If the internal state resistance R_{int} is varied, the I - V curve of memristor starts pointing out from the edges as shown in Fig. 9. The results demonstrate the effect of frequency and the effect of change in internal state resistance. As we increase the internal state resistance, the peak value of the curve does not show variation rather it remains on the same slant with no change in the resistance.

In simple words, if we increase the internal state resistance, in positive region and at maximum voltage and current levels, the resistance value remains same and sweeps more value than its negative counterpart.

Input signal plot for the I - V characteristics shown in Fig. 8 is plotted in Fig. 10. In the plot, sinusoidal signal, V_{in} is given as an input and the internal state of memristor V_{state} is shown, which remains in the positive region. The output voltage is shown as curve V_{output} in the plot. It can be considered as the input current also. The change of that curve is dependent on the internal state resistance.

Behavior Due to Different Input Signals

In this section thorough analysis on memristor is done on different type of signals viz. sinusoidal input, square wave, sawtooth wave, and DC input signals. In the following subsections, I - V characteristics of the memristor for different signals are provided (Singh, 2014). The resistance change with time and voltage are also given in their respective subsections.

Current–Voltage (I - V) Characteristics

Consistent voltage source of amplitude 1.5 V is chosen to study the effects on memristor due to different signals. Voltage of amplitude 1.0 V is given to study the I - V characteristics for DC input signal, the voltage is taken as an absolute value for symmetry. The current–voltage (I - V) plots of memristor is given in Fig. 11 for sinusoidal input. It shows that for the input 1.5 V sinusoidal input the memristor sweeps current of 0.18 mA if the frequency f is 1 Hz and the lissajous figure is symmetrically same in positive and negative region that represents a working memristor (Cassuto *et al.*, 2013).

In Fig. 12, the square wave of frequency f 1 Hz is given with peak amplitude of 1.5 V. The plot shows some interesting results, that at the peak amplitude of voltage in either polarity, the resistance is memristor changes abruptly towards origin or low resistance state. One thing that is fascinating is the current I sweep. For square wave, the maximum current sweeps in 1.5 mA region that is much higher than other input signal types.

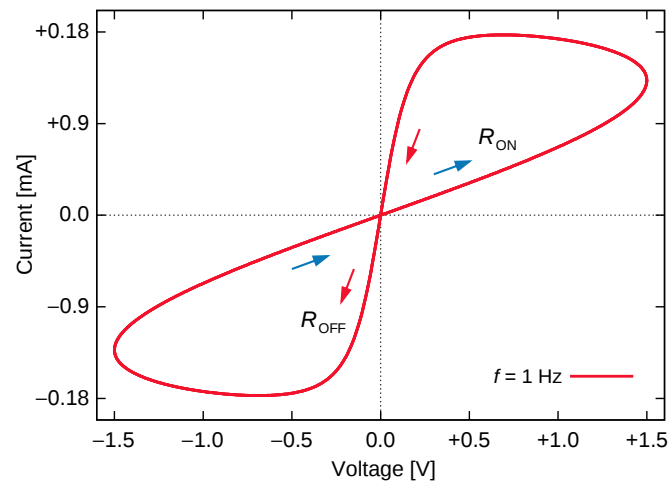


Fig. 11 I - V characteristics plot for sinusoidal input. Singh, T., 2014. Design and analysis of Memristor: The missing circuit element. Master's Thesis. Disp. Electron. Elect. Eng., Lovely Professional University, PB, India.

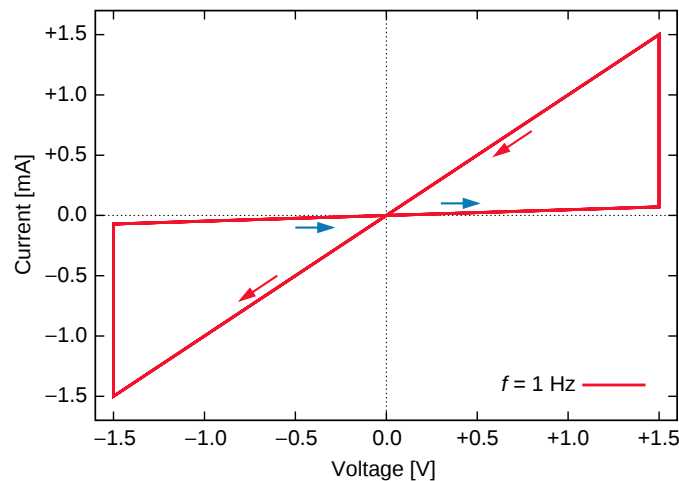


Fig. 12 I - V characteristics plot for square input. Singh, T., 2014. Design and analysis of Memristor: The missing circuit element. Master's Thesis. Disp. Electron. Elect. Eng., Lovely Professional University, PB, India.

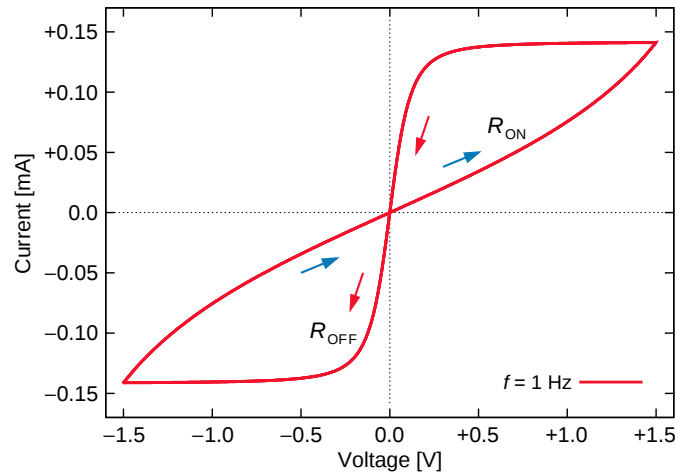


Fig. 13 I - V characteristics plot for **sawtooth input**. Singh, T., 2014. Design and analysis of Memristor: The missing circuit element. Master's Thesis. Disp. Electron. Elect. Eng., Lovely Professional University, PB, India.

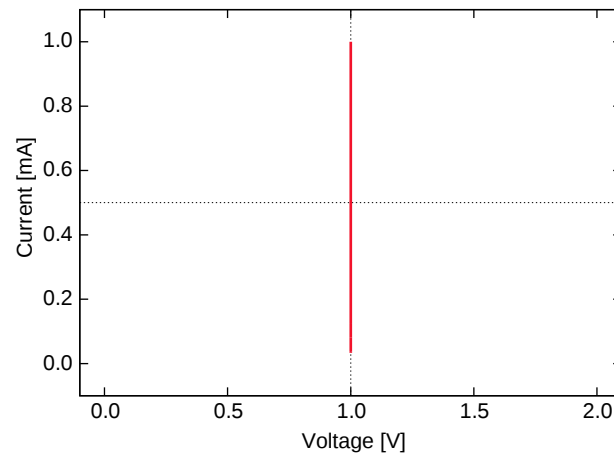


Fig. 14 I - V characteristics plot for **DC input**. Singh, T., 2014. Design and analysis of Memristor: The missing circuit element. Master's Thesis. Disp. Electron. Elect. Eng., Lovely Professional University, PB, India.

Fig. 13 results in the characteristics if sawtooth wave is applied of 1.5 V amplitude and 1 Hz frequency f . The plot states that the I - V characteristics of sawtooth wave is almost similar to that of sinusoidal plot given in **Fig. 11**. The matter of the fact the curve gets pointed and the structure becomes leaf-like only because of the sawtooth wave that abruptly starts decreasing after the peak amplitude. **Fig. 14** shows the I - V curve for DC input. The hysteresis curve collapses to one particular point at 1.0 V and the maximum current sweeps till 1.0 mA only in positive region. The memristor works well for all the input signals except DC signal. Because the memristor is frequency dependent.

Different Input Signals

The input signals, that are used to plot the I - V characteristics are shown in the figures below with respect to time. Current in mA and Voltage in V are plotted for all the signals and demonstrated their dependency on frequency.

Sinusoidal input signal plot is shown in **Fig. 15**. The plot demonstrates the peak amplitude of voltage and current signal with respect to time in seconds. **Fig. 16** shows the rectangular pulse input signal given to generate I - V characteristics as shown in **Fig. 12**. The current reaches at the peak amplitude on positive side during the leading edge transition of the signal and on the negative side during the trailing edge transition of signal from negative to positive. The signal is shown for time 4.0 s.

Input sawtooth signal is actually a triangular signal with peak amplitude of 1.5 V in positive and negative region as shown in **Fig. 17**. The input current is also shown for the maximum amplitude of 0.15 mA. The current changes as the signal changes in a slope. The DC input signal is shown in **Fig. 18**. The plot points out that when the input of DC 1.0 V is applied, the currents starts decreasing towards 0.0 mA range. This is the fact that DC does not carry frequency, hence it affects the I - V characteristics. The figures are arranged to clearly differentiate the signals that are taken as input.

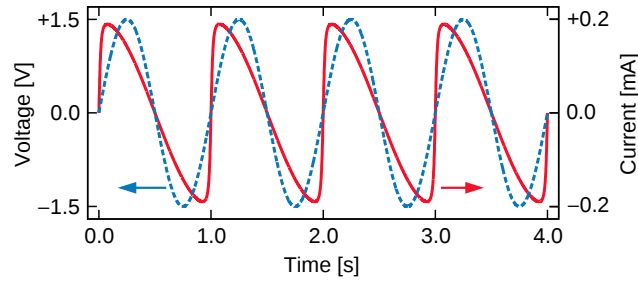


Fig. 15 Sin input voltage and current signal plot.

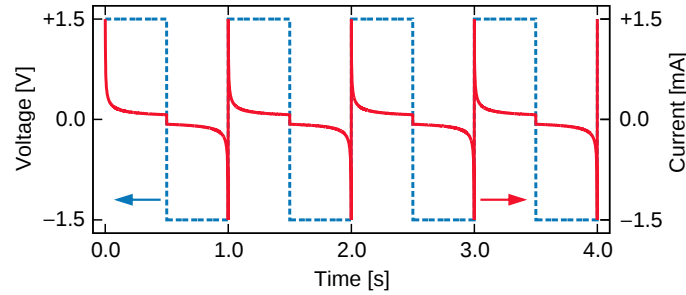


Fig. 16 Square input voltage and current signal plot.

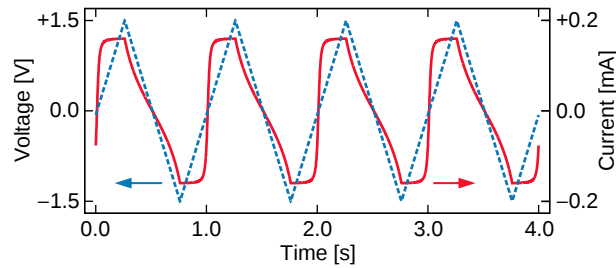


Fig. 17 Sawtooth input voltage and current signal plot.

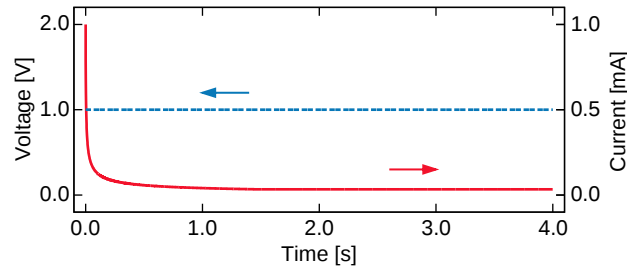


Fig. 18 DC input voltage and current signal plot.

Variation in Resistance With Time (t)

The change in resistance with the applied voltage is the basic phenomena of memristor. The internal resistance varies that can be demonstrated from the I - V characteristics given. But the actual change in resistance with the change in time is shown. The resistance variation is plotted for all the input signal types. **Fig. 19** shows the change of resistance when sinusoidal signal is applied. This results in the peak resistance of 16 k Ω . **Fig. 20** shows the variation of resistance with respect to time. At the abrupt change in input signal, the resistance reaches at peak exponentially and vice versa, the resistance starts decreasing. The maximum resistance of the device when square wave is applied is 16 k Ω .

Fig. 21 shows the resistance variation when sawtooth signal is applied. The resistance change is almost equivalent to that of when sinusoidal input is applied. **Fig. 22** shows change in resistance when DC input is applied. The resistance reaches at peak when the current reaches 0.0 A. As the current is approaching towards its origin, the resistance increases

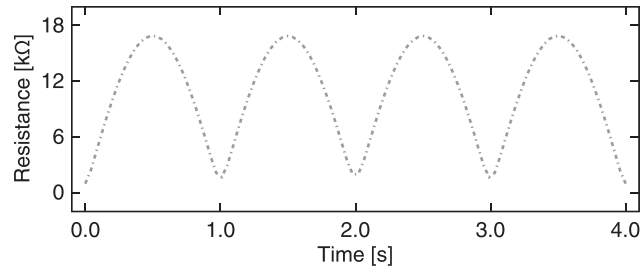


Fig. 19 Resistance variation of 16 kΩ for **sinusoidal input**.

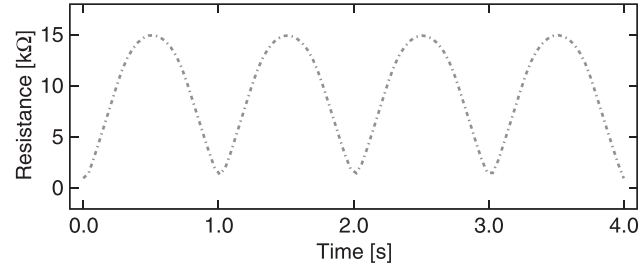


Fig. 20 Resistance variation of 18 kΩ for **square input**.

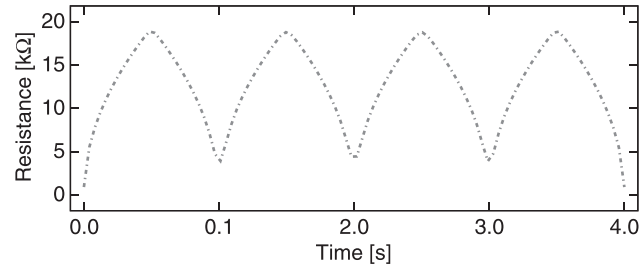


Fig. 21 Resistance of 16 kΩ for **sawtooth wave**.

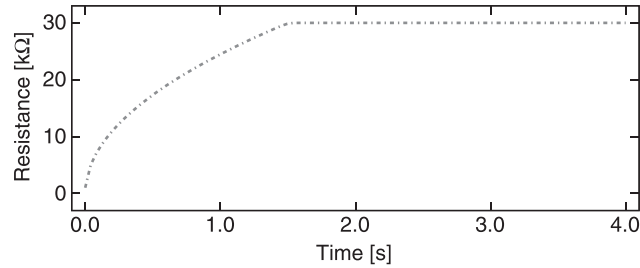


Fig. 22 Resistance of 30 kΩ setup for **DC input**.

exponentially. The peak value of the resistance when DC is applied is 30 kΩ, that is the actual R_{OFF} of the device. From the plots, it can be concluded that for different signal types the resistance change almost remains equal but the slope of resistance changes.

Change in Resistance With the Effect of Voltage (V)

The change in resistance with respect to voltage for different signals are plotted in this section. As per the previous section, the resistance change is totally due to the effect of ionic drift in memristor. [Fig. 23](#) and [Fig. 24](#) show the five resistance change with respect to voltage for sinusoidal and square wave, respectively. [Fig. 25](#) shows the plot when sawtooth wave is applied and [Fig. 26](#) shows the result of resistance change when DC input is provided.

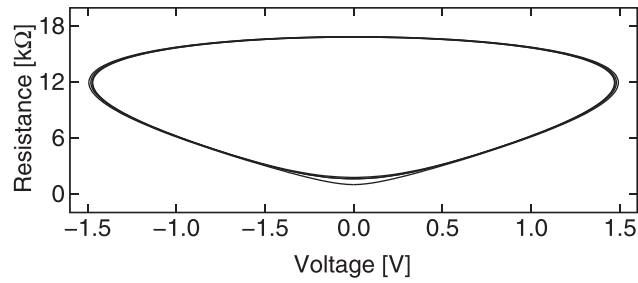


Fig. 23 Resistance vs. Voltage plot for **sin** input.

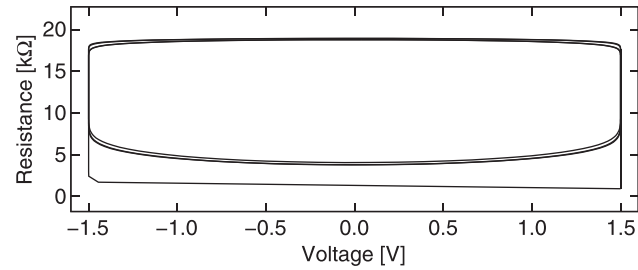


Fig. 24 Resistance vs. Voltage plot for **square** input.

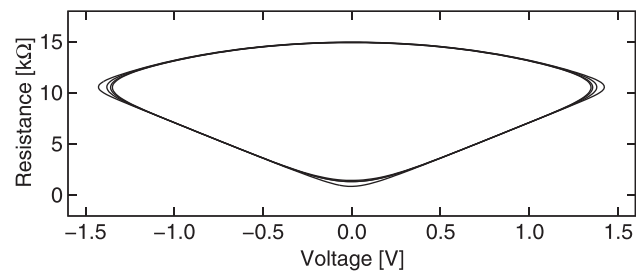


Fig. 25 Resistance vs. Voltage plot for **sawtooth** input.

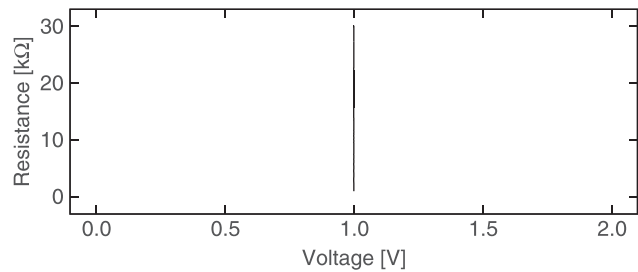


Fig. 26 Resistance vs. Voltage plot for **DC** input.

From the plots it can be said that the resistance change when sinusoidal signal is applied with respect to voltage is almost similar to that of when the sawtooth wave input is provided. The resistance does not vary as per the voltage change for DC input signal.

Types of Memristors

There are few vectors of inquiry researching different types of memristors. The memristor material implementation is very important to how to study their behavior in a memristive system. It is important to understand the basic difference between a memristor as a device, and a memristive system on the perspective of complete system, because one specific type of memristor can highlight specific and different strengths and/or weaknesses, and these can be used in memristive systems for various applications of purpose or scale. Until now, there are currently no datasheets on memristors are available, as the material implementations are experimental and is in initial development stage.

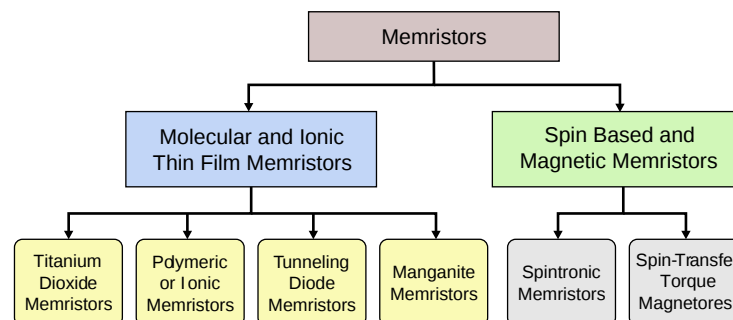


Fig. 27 Flowchart demonstrating the classification of Memristors.

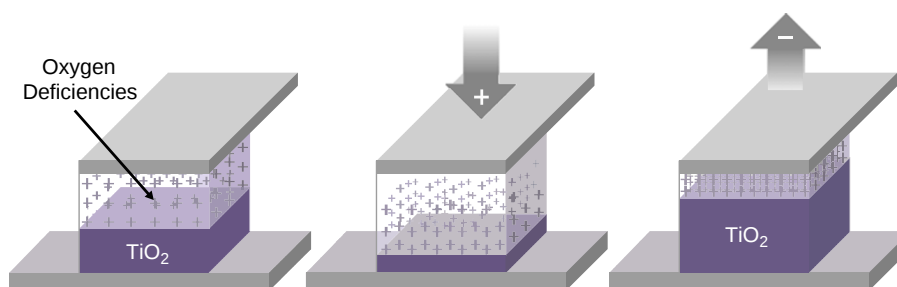


Fig. 28 Oxygen deficiencies and its effect in TiO_2 memristor under the applied electrical field.

In general, for any material, hysteresis, a rate of change of property as objects tends to move from one to another state, is a practical indicator of memristive properties (Ascoli et al., 2013; Yang et al., 2012; Chanthbouala et al., 2012).

Currently the Hewlett Packard (HP)'s version of the TiO_2 substrate-based memristor is the most generally pursued or a generic type of memristor, but the list of various memristor types are shown in Fig. 27. There is a huge variety of systems that exhibit the desired memristive behavior, and more are continuously get discovered as industries begin to build out their own prototypes, research, and manufacturing infrastructures. Classification of different memristors are shown in Fig. 27.

Molecular and Ionic Thin Film Memristive Systems

These are the fundamental type of memristors that primarily rely on different properties of material mostly of thin film atomic lattices that exhibit hysteresis under the application of charge flow (Blanc and Staebler, 1971; Strukov et al., 2008).

TiO_2 memristors

The first practical TiO_2 memristor was developed by HP Labs is basically based on a two-layer thin 'stacked layers' of TiO_2 films, composed of lattices that are symmetrical of titanium and oxygen atoms as shown in Fig. 28. (TiO_2 changes its resistance in the presence of oxygen atoms, that is why it is used extensively in oxygen sensors.) The movement of atoms in these thin films are tied to the motion of electrons in that material, which allows a change of state in the atomic structure of the device or memristor to be specific. The bottom layer acts as an insulating material and the top film layer acts as a conductor via additional oxygen vacancies in the TiO_2 (Prodromakis et al., 2011) material. The oxygen vacancies in the top layer of the material are shifted towards the bottom layer, changing the state or resistance, and thus maintaining a stable state. To access the memristive properties, crossbars made of nanowires are designed above and below of the top and bottom layers of material, so that the charge can be transferred through.

It is quite interesting that R. Stanley Williams at HP Labs came to the material property of TiO_2 of memristive effects in part through his primary interests in the miniaturization of sensor technology for distributed sensing systems.

Polymeric (ionic) memristors

Utilizing the basic properties of different solid-state ionics, one of the component of the structure of material, i.e., the cationic or anionic, is free to move throughout the polymeric structure as a charge carrier. Polymeric memristors extends dynamic doping of inorganic dielectric-based material and polymers to attempt and show hysteresis type of behaviors. Usually, one single passive layer in between of an electrode and a thin film (active) attempt to accelerate the extraction of ions from the electrode. The

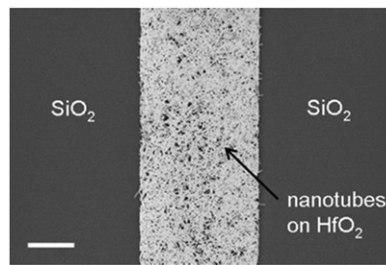


Fig. 29 SEM image of fabricated SiO_2 memristor represents nanotubes on HfO_2 . Carbon nanotubes to replace silicon: IBM (News) 2012. <http://www.kurzweilai.net/>.

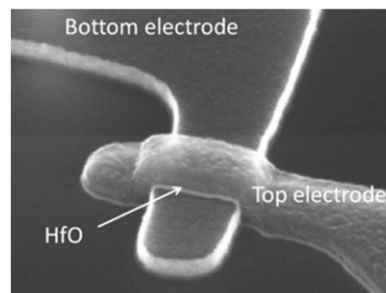


Fig. 30 Fabricated HfO_2 Memristor represents the insulated sandwiched material. Johnson R 2012 IMEC to detail memristor progress at VLSI symposia (News). <http://www.eetimes.com/>.

polymeric terms and ionic terms are often used somewhat loosely and generically (Greenlee *et al.*, 2013).

Manganite memristive systems

A bilayer oxide substrate films based primarily on manganite, in lieu to TiO_2 , Cheng (2011), had shown the describing properties of memristive system at the University of Houston in year 2001.

Resonant-tunneling diode memristors

Certain types of diodes based on quantum-well with designs that are special doping of the spacer layers between the drain and source regions exhibits memristive properties (Balke *et al.*, 2010).

Silicon oxide memristors

Scientists have developed memristive substrates of silicon oxide that promises for transitioning much of the world's current fabrication and production infrastructure to the production of memristor (Yang *et al.*, 2012). Various materials have been investigated that can be feasible for memristors, as the memristor fabricated using silicon dioxide, SiO_2 is shown in Fig. 29 and hafnium dioxide, HfO_2 memristor that have high dielectric constant is shown in Fig. 30.

Spin-Based and Magnetic Memristive Systems

Memristive systems that are Spin-based, as opposed to ionic and molecular nano structure based, rely on the degree of freedom property in electron spin (Wang *et al.*, 2009). In these type of systems, the polarization of electron spin is varied, usually through the movement of magnetic wall that separates polarities, that further allows for the occurrence of hysteresis like behavior.

Spintronic memristors

It is a type of magnetic memristor under the development by various labs, primarily Seagate, is known as a spintronic memristor. It is known that the TiO_2 based memristor change its state by varying oxygen vacancies in between two different layers, varying the resistance state of a spintronic memristor uses magnetization to vary the direction of spin of electrons in two separate sections of device. Basically, the two sections of different spin directions of electrons are kept separately by a moving wall, which is controlled usually by magnetization property, and the relationship of the moving wall dividing the spins of electrons further controls the device's overall internal state change (Wang *et al.*, 2009).

Spin torque transfer (STT) MRAM

Since the late 1990s, the research of MRAM has shown, in some cases, can say the memristive properties. The configuration is well-known as a spin valve, the most simplest structure for an MRAM bit allows for the internal state change. The state or resistance in a memristive spin torque transfer is governed by a spin torque that is induced by a current flowing through a junction (magnetic). It is dependent on the difference in the orientation of spin in-between the two different sides of junction. Depending on the material that is used to build some MRAM bits, the spin torque constructions can show both magnetic and ionic properties and are referred to as 'second-order memristive systems.'

Three-terminal Memristors

As an early outlier from the 1960s, the most prominent technology of electroplating was used to demonstrate the feasibility of a non-solid state, 3-terminal memristor is shown by Bernard Widrow at Stanford. The conductance of the device was described as being governed by the time integral of current i . It is quite interesting to note that the research done was a part of a much larger project into the mathematics of modeling of early neural networks. The Adaptive Linear Element of Widrow and his student named Ted Hoff is a one layer neural network based on the McCulloch Pitts Neuron, and that demonstrates that even in the early days, the modeling of memristive systems was very closely related to neural learning algorithms.

Applications

The question is that, Which Memristive applications are currently on the horizon, and how close are they all to reality? We sneak peak at a survey of memristor applications and technologies related to memristors, beginning from what the initial devices will look like, and Where they might see some potential? The few major applications are given below:

Nonvolatile Memory Applications

Memristors or the memristive systems can retain states, and data, even in totally power-off modes. Nonvolatile random access memory (NVRAM) is pretty much the first memristor-based application we will be seeing in near future. There are already memristors in fabrication now that are just 3 nm wide. The most common crossbar latch memory that is developed by HP is reportedly currently about one-tenth the speed of current DRAM (Ho *et al.*, 2009). The fabrication prototypes state is read with alternating current, such that the value that is stored should remains unaffected. Rosy colored industry analysts shows that there is manufacturing concurrence that these memristor-based flash memory or solid-state drives (SSD) competitors could start coming up in consumer market within approximately 2 or 3 years.

Low-Power and Remote Sensing Applications

The circuits that complementary to the memristor that allow for the storage of charge, coupled with mem-capacitors and mem-inductors can possibly allow for nano scale memories that consumes low power and distributed state storage as an extension of NVRAM. These claims are currently all hypothetical in terms of development and time to market (Sarwar *et al.*, 2013).

Crossbar Latches as Transistor Replacements or Augmentors

The higher power dissipation of MOSFETs and transistors has been a thick barrier to both microprocessor controller development and miniaturization (Kuekes *et al.*, 2005; Strukov and Likharev 2007). Solid-state memristors can possibly be combined into devices known as crossbar latches, that could replace MOSFETs in near future computing architectures, taking up a much smaller area as compared to current generation devices. There are few difficulties in this area also. Although, the benefits these postulations could target a lot of money in their research and development. Unless a war amongst industry giants based on competition becomes one of those patent prominent, where companies buy out technology advancements to bury them (Deng *et al.*, 2013) and have profited greatly (Chang *et al.*, 2011b; Corinto and Ascoli, 2012).

Analog Computation and Circuit Applications

There was a record of electrical and mathematical engineering that was primarily abandoned to stasis in the 1960s, as digital analogy and IT/computers rose to dominance. Computations basically analog embodied a large area of research that, unfortunately, were not as reproducible, scalable, and/or dependable as their digital counterparts (Greenlee, 2011; Greenlee *et al.*, 2013). However, there are still some highly important areas of modeling and engineering problems that require highly complex and

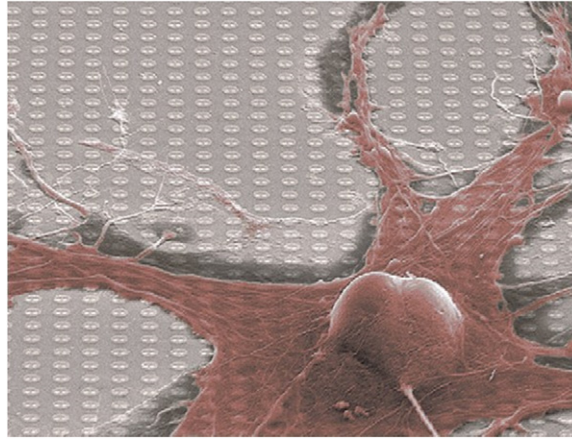


Fig. 31 Artificial neural biological tissues based on memristor. Life Sciences Innovations: Mikroelektroden und Neurochips. LABOnline. <http://www.labo.de/>.

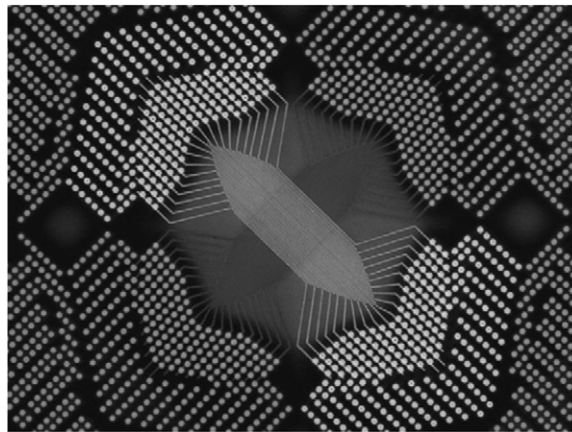


Fig. 32 Prototype of Neuromorphic memristor with CMOS integration. 2013 DARPA SyNAPSE Program. <http://www.artificialbrains.com/>.

extremely difficult workarounds to model it digitally in part, that is because these map economically onto their corresponding analog models. The preliminary work of N. Wiener has already started revisits only after the analog and digital split in-between him and J. vonNeumann (Chanthbouala *et al.*, 2012; Cheng, 2011; Chua, 1969; Singh, 2015). Analog was great due to its instantaneous nature, but that also required management for, out of scope scalability what even the most complex initial computers based on digital vacuum tube could provide. The applications of memristors will now allow us to rethink a lot of left analog science that was somehow abandoned in the 1960s (Lee and Nickel, 2012; Singh, 2015).

Neuromorphic and Biological Systems

The need of analog science explained above has to do much with advances in cognitive psychology and modeling of artificial intelligence, machine learning, and advancement in neurology (Jo *et al.*, 2010a,b; Perez-Carrasco *et al.*, 2010). The activities like the ability to map the brain of people under CAT, MRI, and EEG scans is taking us to a trove of knowledge and information about the functionality of our brains. But the modeling of an extremely complex system like brain using ratiocinated mathematics seems like using linear algebra to model complex calculus (Chang *et al.*, 2011a). The recent experiments show that the circuit, subjected to periodic pulses or train of pulses, adapts and anticipates the next pulse that is about to occur, identical to the conduct of the slime-mold *Physarum polycephalum* periodic timing. Artificial neural biological tissues based on memristor is shown in Fig. 31.

Due to the fact that it is subjected to the periodic changes of environment. The recent research on memristor, cat brain is also getting a lot of attention. These type of adaptive circuits and systems find applications anywhere from complex pattern recognition to advance neural networks as shown in Fig. 32 (Serrano-Gotarredona *et al.*, 2013; Kim *et al.*, 2011).

Programmable Logic and Signal Processing

Memristor-based signal processing, logic, and a variety of control system are out there, waiting for the tiny microchips/ICs to fall where they may (Pershin and Di Ventra, 2010). The applications of memristor and memristive systems in these areas will remain mostly the same because, it only need a change in the underlying physical architecture thus allowing their capabilities to enlarge further. However, to the point where its applications will mostly be unrecognizable as related (Biolek *et al.*, 2012).

Summary

The nanoscale feature size of memristor makes it an ideal candidate for future high-speed computing circuits and devices. Memristor can remember the last state, is a passive two-terminal device, its terminals can be interchanged. Its unique $V-I$ characteristics makes it a totally different device. Memristor can be integrated with CMOS to implement with current generation circuits. Fabrication of memristor is simpler than CMOS. With nanoscale size, low power consumption, Moore's law seems valid for coming years. The invention of memristor opens door to many potential applications which was otherwise seems impossible. Various types of memristors has been proposed by many researchers with advantages over one another. There is a need of researchers in the field of materials, circuit implementations, VLSI, nanotechnology, and computer science to develop applications from this amazing device.

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Industrial Fabrication of ZnO Varistor: Leveraging the Powder Processing Parameters

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Abstract

The performance and functional reliability of zinc oxide (ZnO) varistor are dependent on various process parameters of which the powder processing aid binder, the spray drying parameters, particle size and its distribution are crucial in powder processing step. The functional reliability and failure mode were significantly affected by each of the processing steps. Both the mechanical and electrical performance were improved with the use of new binder. Not only that, the reliability of varistor disks was also enhanced. The distribution of particles in varistor powder also influenced the properties. Though the varistors fabricated from narrow distribution with fine powder could increase the breakdown voltage but the overall performance was poor. Hence, widely distributed spray dried powder with higher fraction of coarse particles is recommendable for varistor fabrication.

The key term zinc oxide varistor is used for a high transient over-voltage suppressor which is fabricated from the electronic ceramic material zinc oxide. This is characterized by its excellent non-ohmic properties in current voltage relationship. The non-linear region is the heart of the device which clamps the voltage upon the application of transient surge. The flatter the non-linear region, the better the device. Addition of multiple dopants (additives) can improve the intrinsic non-linearity and reliability of zinc oxide further.

Key term energy absorption capability is the second most important parameter to judge the performance of zinc oxide varistor. The energy is calculated as $\text{J}\cdot\text{cm}^{-3}$, where the higher value demonstrates better energy absorption by the device from upcoming transient surge and enhanced protection for power transmission line. Grain size and its distribution and less flaws in the fired disks can improve the performance in terms of energy absorption capability.

Introduction

A ZnO varistor is a semiconducting device possessing non-linear current-voltage (I - V) characteristic with a symmetrical sharp breakdown similar to that of a zener diode (Matsuoka, 1971; Gupta, 1990; He, 2019). But unlike a diode, a varistor can limit over-voltages in either polarity, thus, giving rise to I - V characteristic which is analogous to the back to back Schottky diodes. This has enabled it to provide an excellent transient suppression performance. It is a preferred approach to protect electrical, electronic and power distribution, and transmission circuits from destructive voltage levels induced by lightning impulse or switching surges. It was introduced by Matsuoka (1971) in early 1970s, and so far it has been the most important material employed as the base for ceramic systems in the commercial production of varistors (Aguilar-Martínez *et al.*, 2016). Currently wide ranges of varistor products are available in the market (Transient Voltage Suppression Devices, 1995; Metal Oxide Varistor: Littlefuse Voltage Suppression). The application parameters associated with various regions of the I - V curve are critical in design and operation of the surge protector. The product should have a low value of clamping ratio, a high value of non-linear coefficient, a low value of leakage current, high energy absorption capability leading to longer varistor life (Nahm, 2016; Topcagica *et al.*, 2018).

The use of ceramic as transient over-voltage protection is the development of electronic ceramics. There are two major categories of transient over-voltage suppression in electronic power systems. One is based on the principle of attenuating the transient signals and the other is on diverging sensitive load and thereby limiting the residual voltages. The first category suppressor is filter (capacitor) which is inserted in series within the circuits and attenuates the transient (high frequency) and allows the signal and power flow (low frequency) to continue undisturbed. The second type of suppressor is a crowbar type device.

Zinc oxide varistor is a high transient over-voltage suppressor. It has very large suppression capabilities, which are considered as the combination of both the feature of silicon-zener diodes and silicon carbide varistor. This device is characterized by the excellent nonlinear current-voltage behavior (Amotch Co., 2003) as shown in Fig. 1. The nonlinear feature of the ZnO varistor is attributed to the grain boundary phenomenon, and this is the intrinsic property of the ceramic material.

ZnO varistor is processed by the conventional powder processing route where the processing aids, dopants, particle size and its distribution, compaction, sintering, passivation and electroding play an important role. Thus, various aspects of processing aids are included here.

Processing of Arrester Block

Zinc Oxide varistors produced in the form of cylindrical shaped blocks are often called arrester blocks. These are fundamentally ceramic materials, processed from a number of metal oxide powders. The basic material used to manufacture metal-oxide varistors

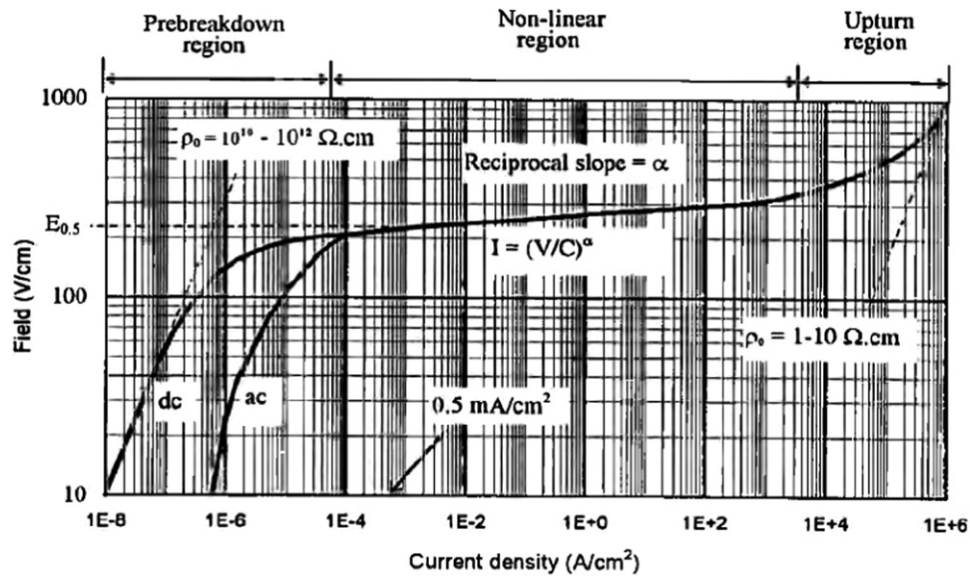


Fig. 1 Current-voltage characteristics of the ZnO varistor.

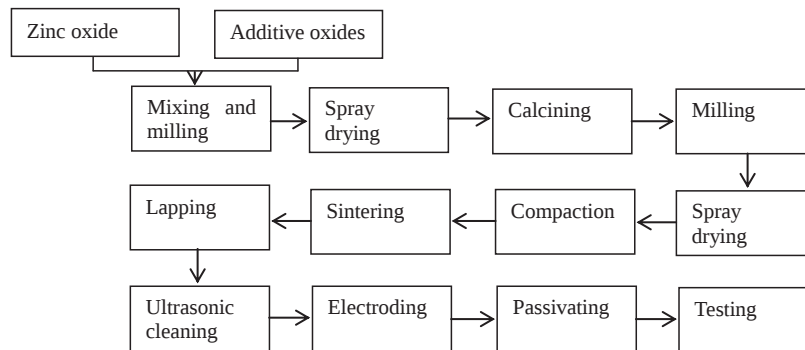


Fig. 2 Fabrication procedure of the ZnO arrester block.

are pulverized, very finely grained ZnO with particle sizes of about $1\ \mu\text{m}$, to which as many as 10 or more cations are added in the form of fine oxide powders. Its actual composition differs from manufacturer to manufacturer. The proportion by weight of all the additives together is about 10%, with the share of the individual components ranging from ppm to percentage level. The purity and fineness of the metal-oxide powders and the homogeneity of the mixture are, therefore, of immense importance for the quality of the end product.

To achieve the required homogeneity in the powder it is treated in several processing steps, after which the mixture in the form of slurry has to be spray-dried to obtain the dry granulates necessary for pressing. The resulting spheroidal granulates are about $50\ \mu\text{m}$ in mean diameter having a wide distribution. Majority of the varistor devices are processed from this kind of powder except some category such as multilayer varistors which are made from a slurry paste. The manufacturing steps to fabricate the arrester blocks is depicted in Fig. 2. However, these steps may vary depending on the sequences desired.

The spray-dried powder in the form of granulates is compressed into disc-shaped blocks with approximately 55%–65% of their theoretical density. Pressing is performed by a uniaxial double action compaction technique. Sintering of the disks is performed by a conventional profile having a peak temperature ranging between 1100 and 1400°C , and a total sintering cycle time usually ranging between 24h and 48h. The peak-sintering temperature often dictates the cycle-time. Therefore, sometimes the cycle-time may exceed 48h. The sintered body takes the shape of a rigid cylinder possessing theoretical density of more than 95% with shrinkage ranging between 15% and 20%. ZnO varistors undergo a liquid-phase sintering process. During this process, the bismuth oxide melts to form the liquid-phase which dissolves, at least in part, the other cations and presumably promotes their uniform distribution. The liquid-phase also favors the grain growth and dense sintering. Spinel precipitates, on the other hand, inhibit grain growth and help generate a uniform distribution of the ZnO grain size.

Binder in Processing of ZnO Varistor Powder

The binder used in the processing plays an important role in achieving the powder of the ZnO varistor. Apart from affecting the powder characteristics, green strength and density gradient of the as-pressed cylindrical disks, the grain growth during the sintering cycle, and subsequent microstructure development are also affected by the binder system. The green and the fired body, homogeneity, grain size, porosity, varistor chemistry are identified to affect the performance of the device remarkably (Nies and Messing, 1983; Dilima and Reed, 1981).

Poly-vinyl alcohol (PVA) plasticized with poly-ethylene glycol (PEG) is the most commonly used binder in the electro-ceramic industry for dry pressing. The binder is available in solid form and it is necessary to make an aqueous solution before adding to the slurry. In addition, the hygroscopic nature of the binder causes to change in the physical property of the agglomerates with the variation of environmental humidity (Brewer *et al.*, 1980). Moreover, gelating is associated with PVA which is attributable to generate pinholes in the varistor block during sintering, thereby seriously confining the electrical performance of the disc.

Latex binders are from the resin group of acrylics. It is available in emulsion form and are extremely hydrophobic and making themselves insensitive to the change of humidity. Nyberg *et al.* (1988) have studied the advantage of acrylic latex in the processing of homogenous granules of alumina by spray drying. More uniform green and fired body can be obtained by the use of acrylic latex. Wu and McAnany, Wu *et al.* (2008) have concluded that the acrylic binder can produce green compacts of very high green strength because of strong interactions of carboxylic acid group with ceramic powder, and polymer to polymer interaction by hydrogen bonding within the carboxylic group. Commercially available latex binder (Duramax, Rohm and Haas) B-1007, B-1020, B-1023, B-1000 and their blends with the identification of binder, and solid content in slurry is presented in Table 1. The use of suitable binder can improve the physical properties with better *I-V* characteristic and consistent energy absorption capability. Thus, better arrester blocks can be secured for more demanding applications with a higher system functional reliability.

Effects of Binder On Green and Fired Strength

Effect of binder on the green strength of the disc is depicted in Fig. 3. There is a wide variation in green strength being lowest with the PVA and highest with Ltx E. Latex binder contains carboxylic acid group and the presence of interchain hydrogen bonding within the group is responsible for polymer to ceramic and polymer to polymer bonding. This type of bonding is not found with the PVA and it is assumed that this type of bonding will provide more strength (Brewer *et al.*, 1980; Nyberg *et al.*, 1988). The increase of binder content, therefore, increases the green strength. The disks made with the powders derived from slurries with higher percentage of solid exhibited greater strength as shown in Fig. 4. More percentage of fine particles and higher granule density of powder due to the higher level of solid content have led to increase the green strength (Brown, 2004; Begum *et al.*, 1998; Rumpf, 1962; Akdogan *et al.*, 1999).

Table 1 Identification of the binder systems, type, binder level and solid contents

Commercial name of binder (Duramax)	B-1007	B-1007 + B-1000	B-1020	B-1020 + B-1000	B-1023	B-1020	B-1020	B-1020	B-1020	B-1020
*Coded name of binder	Latex A	Latex B	Latex C	Latex D	Latex E	PVA	Latex C1	Latex C2	Latex C3	Latex C4
Binder (%)	1.30	1.30	1.30	1.30	1.30	1.30	1.00	1.60	1.00	1.30
Solid (%)	72.0	72.0	72.0	72.0	72.0	72.0	72.0	72.0	80.0	80.0

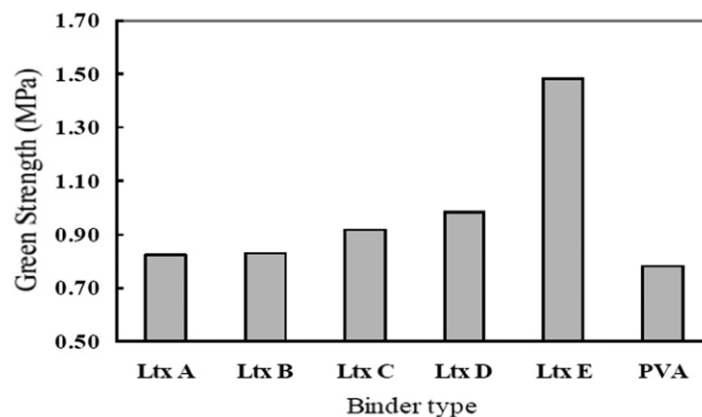


Fig. 3 Green strength of varistor disks with different binder system.

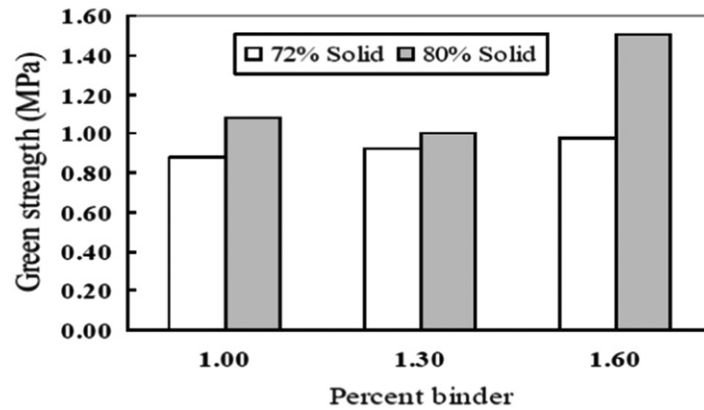


Fig. 4 Green strength of varistor disks at different binder and solid concentrations.

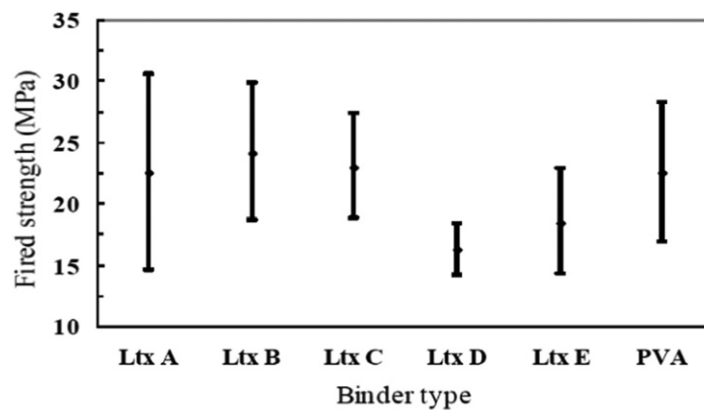


Fig. 5 Fired strength of varistor disks with different binder systems.

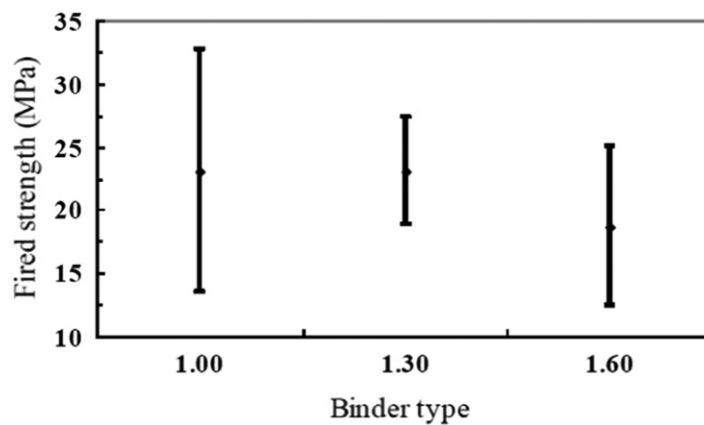


Fig. 6 Fired strength of varistor disks produced from powder at 72% solid concentration.

The influence of binder on the strength of fired disks is demonstrated in [Fig. 5](#). There are a wide variation of strength and the highest being obtained with Ltx B. The strength of the fired disks with Ltx C is also higher than that of PVA. The consistency of the strength was also higher than that of Ltx B, and this can be attributed to the presence of fewer flaws in the fired body as interpreted from Weibull Modulus, m , for fired strength ([Begum and Hashmi, 2005a](#)).

The fired strength was changed significantly with the variation in the levels of binder at lower solid concentration as shown in [Fig. 6](#). The higher strength was obtained at 1.3% binder level with a low value of standard error. While, enhanced fired strength was obtained at the higher solid concentration for 1.0% binder level as illustrated in [Fig. 7](#).

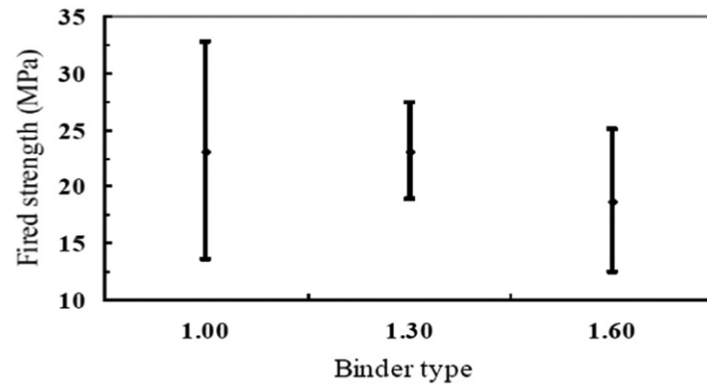


Fig. 7 Fired strength of varistor disks produced from powders at 80% solid concentration.

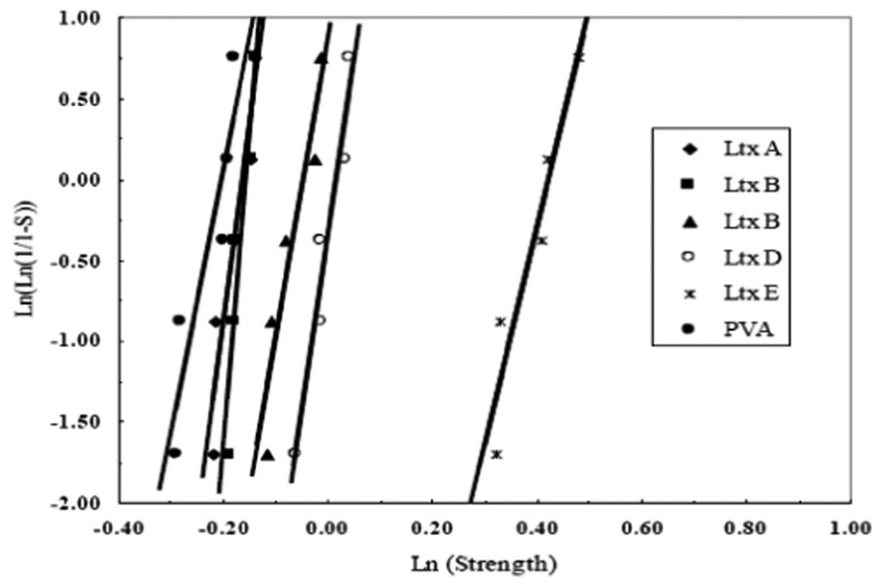


Fig. 8 Weibull plot of green strength of disks with different binder systems.

Weibull Parameters and Reliability

There are two classes of theories to predict the strength of brittle materials. The first is derived from Griffith's flaw theory, (Begum and Hashmi, 2005a) which assumes the presence of flaws of a specific shape, and there is always one with least favorable orientation and the crack growth from this flaw causes failure. The second class is statistical but it fails to specify the nature of flaw. In ceramic, there are a range of flaw sizes which results in a corresponding variation in strength. The most popular means of characterizing the flaw distribution is by Weibull approach (Griffith, 1924).

The probability of failure is predicted by dividing the total volume into many small volume elements, each element has a probability of failure. The probability of survival of the part as a whole is obtained by multiplying the probabilities of survival of all the elements. It is based on weakest link theory, (Batdorf and Heinisch, 1978) which assumes that a given volume of ceramic under a uniform stress fail at the most severe flaw. If the solid is imagined to be divided into n volume elements for which the individual probability of rupture are $S_1, S_2, \dots, S_n$, then the Weibull parameters σ_o , normalizing stress, and m , Weibull modulus, which determine the scattering of the data, can be calculated from the following equation:

$$\ln\left(\ln\frac{1}{1-S}\right) = \ln V - m \cdot \ln \sigma_o + m \cdot \ln \sigma \quad (1)$$

where S is the probability of rupture. This was calculated from the number of specimen under test, by giving each specimen a rank after sorting the stress values from the tests in an ascending order:

$$S = \frac{i}{N+1} \quad (2)$$

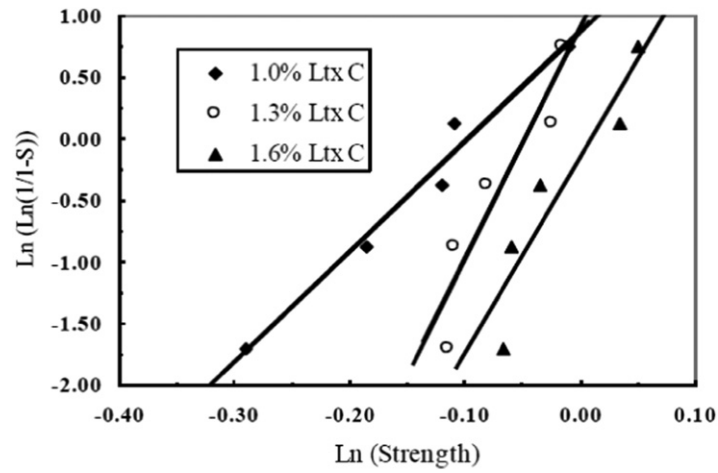


Fig. 9 Weibull plot of green strength of disks with different levels of binder at lower solid concentration.

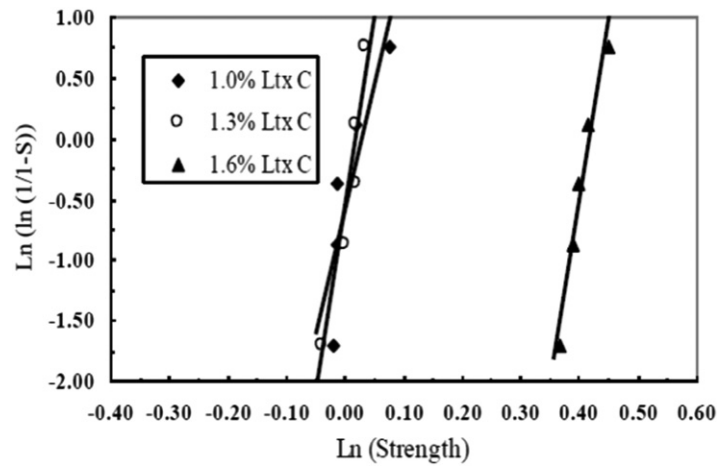


Fig. 10 Weibull plot of green strength of disks with different levels of binder at higher solid content.

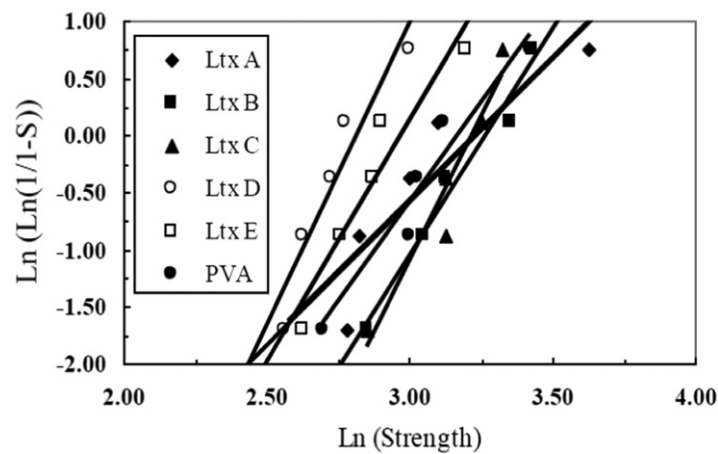


Fig. 11 Weibull plot of fired strength disks with different binder systems.

where i is the test rank and N is the number of tested specimens. The tensile strength measured by the diametrical compression test in MPa was used to calculate the probability of failure using Weibull theory of strength of brittle materials. Weibull distribution for the green and fired compacts containing different types and levels of binder, and different solid concentration are shown in

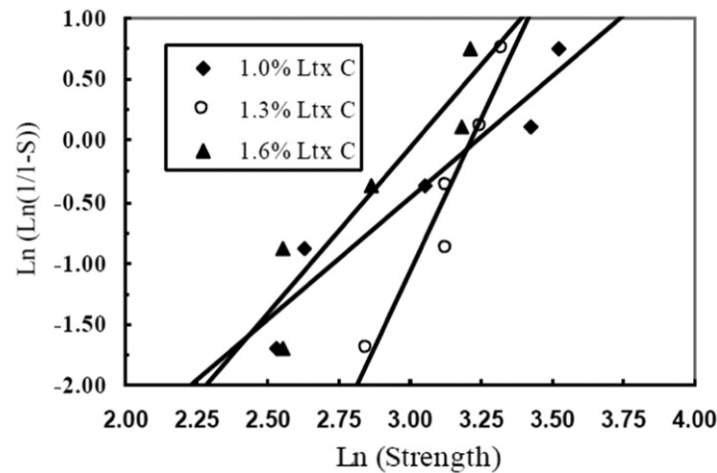


Fig. 12 Weibull plot of fired strength of disks with different levels of binder at lower solid content.

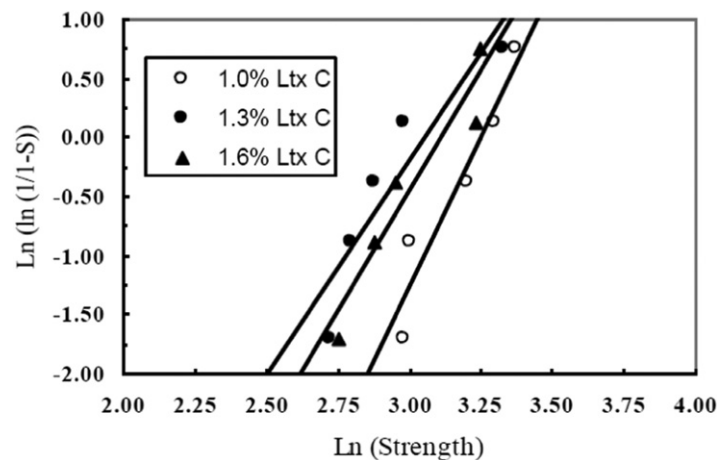


Fig. 13 Weibull plot of fired strength of disks with different levels of binder at higher solid content.

Table 2 Values of weibull parameters

Disc type	Weibull constant	Coded identification of binder										
		Ltx A	Ltx B	Ltx C	Ltx D	Ltx E	PVA	Ltx C1	Ltx C2	Ltx C3	Ltx C4	Ltx C5
Green	σ_o	0.85	0.86	0.96	1.0	1.5	0.81	0.92	1.02	1.02	1.03	1.5
Green	m	24.7	55.6	19.6	39.2	20.3	16.8	7.7	15.3	25.3	23.4	40.5
Fired	σ_o	25.8	26.6	24.8	17.3	20.1	24.5	27.3	21.2	26.1	22.0	23.7
Fired	m	2.44	3.80	4.88	5.16	4.12	3.2	1.98	2.68	6.9	3.44	3.56

Figs. 8 to 13. The plots were used to calculate the normalizing stress, σ_o and Weibull modulus, m . The calculated values are summarized in **Table 2**.

The Weibull modulus, (m) and the normalizing stress, (σ_o) were found to be higher for the same condition (Begum and Hashmi, 2005a). The higher fired strength might be related with the higher green density, as it is thought that highly dense green body would introduce fewer flaws in the fired body.

Effects of Binder on Electrical Properties

The useful varistor parameters such as nominal voltage, watt-loss, clamp ratio, non-linear coefficient, and energy absorption capability were evaluated for the varistors prepared from powder with different binder systems. Nominal voltage was found to be significantly influenced by the type of binder present in the powder. The low slurry viscosity with Ltx C resulted finer atomization.

As a result smaller particles were produced that consequently raised the number of grains. Non-linear coefficient and clamp ratio were also improved for the varistors made from powder containing Ltx C (Begum, 1996). The influence of binder its level and solid concentration had influence on the energy absorption capability of the varistor.

Nominal voltage

Nominal voltage at current density 0.6 mA/cm^2 is illustrated in Fig. 14. The powder processed with Ltx E gave the highest value. But the influence of Ltx C is quite high in comparison to PVA. The change in nominal voltage with the change in binder and solid concentration is given in Fig. 15. The value decreased for the change of binder level from 1.0% to 1.3% but rose again at 1.6% binder level for both low and high solid concentrations. The deflocculating nature of the binder Ltx C caused finer atomization. As a result, smaller particles were produced which increased the grain number during firing and consequently raised the nominal voltage (Richerson, 1982; Meng *et al.*, 2019).

Watt-loss

The watt-loss is presented in Table 3 for varistors made from powder with different binder systems. Lower watt-loss before the application of high amplitude short duration (HASD) pulses with Ltx C may be due to the presence of sodium in ppm level. The ICP (inductively coupled plasma) analysis of remnant ash for different binder systems indicates that the main component of the ash is sodium and its amount is high for Ltx C binder (Chorona *et al.*, 2015; Gupta, 1986). The sodium atom acts as an amphoteric dopant which can occupy both the lattice and interstitial sites of zinc oxide grains and is responsible to reduce the grain boundary resistivity by decreasing the donors in the grains and thereby, the joule heating (Bowen and Avella, 1983). However, after the application of pulse, the higher watt-loss was obtained for the varistor made with powder having lower level of Ltx C and higher solid concentration in slurry, that is, with Ltx C3. Due to lower level of binder, less sodium remains into the varistor after firing and the presence of sodium up to certain extent can occupy the position of interstitial zinc ion in the depletion layer and promote the stability of the device (Bowen and Avella, 1983).

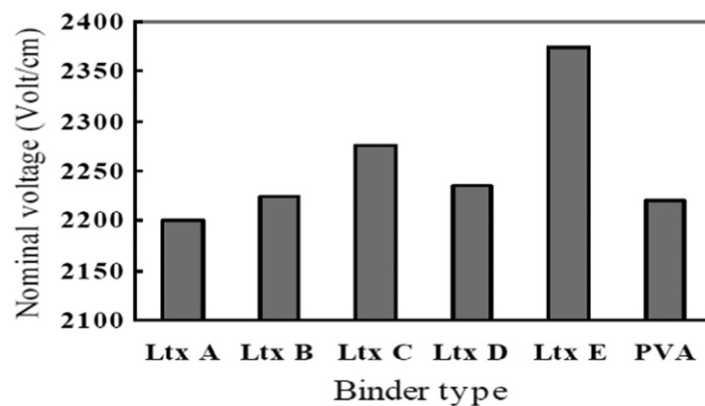


Fig. 14 Nominal voltage of varistor disks with different binder systems.

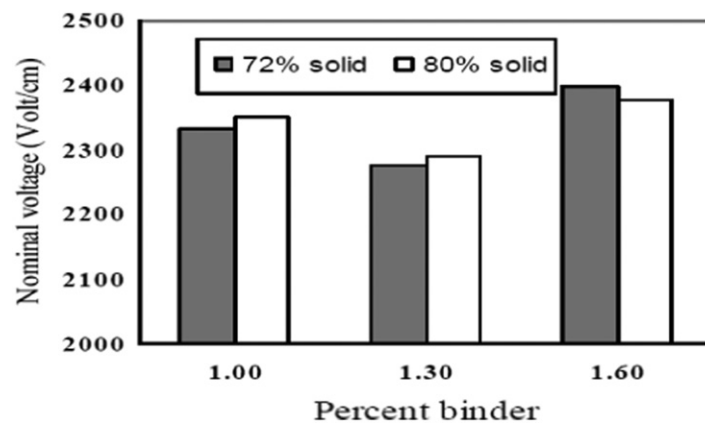
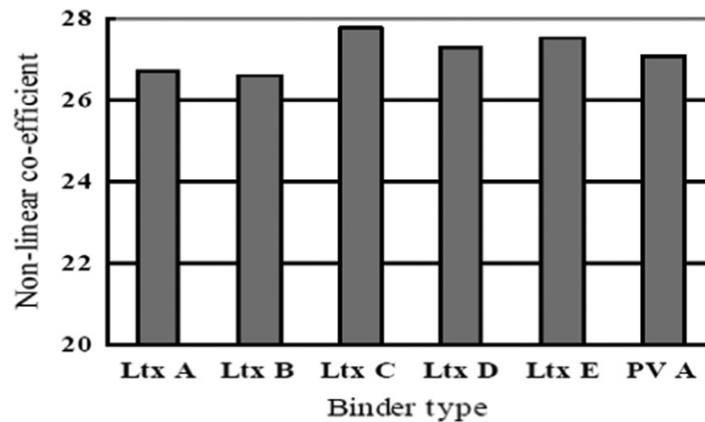


Fig. 15 Nominal voltage of varistor disks at different level of binder and solid concentrations.

Table 3 Watt-loss and clamp ratio of varistors with different binder systems

Binder in varistor powder	Watt-loss $\times 10^3$ ($W\text{ cm}^{-3}$)			Clamp ratio	
	Before shot	After shot		@ 50 μA -1 mA	@ 1 mA-1 KA
		Forward polarity	Reverse polarity		
Ltx A	16.0	15.0	17.0	1.17	1.68
Ltx B	14.0	17.0	17.0	1.16	1.68
Ltx C	12.0	16.0	17.0	1.14	1.66
Ltx D	15.0	15.0	16.0	1.15	1.67
Ltx E	13.0	14.0	15.0	1.14	1.66
PVA	15.0	18.0	19.0	1.16	1.67
Ltx C1	14.0	15.0	17.0	1.15	1.66
Ltx C2	11.0	14.0	15.0	1.12	1.65
Ltx C3	13.0	25.0	25.0	1.08	1.63
Ltx C4	14.0	15.0	15.0	1.14	1.68
Ltx C5	11.0	14.0	14.0	1.06	1.64

**Fig. 16** Non-linear co-efficient with different binder systems (72% solid, 1.3% binder).

Clamp ratio

The clamp ratio was not significantly affected by the binder as seen from [Table 3](#). But a lower value was obtained both at pre-breakdown and breakdown regions with Ltx C and Ltx E. However, the lowest clamp ratio was obtained with Ltx C3. The effect may be attributable to the larger grain size reducing the clamp voltage ([Roya et al., 2018](#)).

Nonlinear coefficient

The non-linear co-efficient of varistors produced from powder with different binder systems is shown in [Fig. 16](#). A high exponent is obtained with Ltx C. This is due to sodium incorporated by the binder within the varistor. Sodium acts as a donor and it can decrease grain resistivity at high current density and lower the clamp ratio. The lower the value of clamping ratio, the higher the non-linear coefficient is. The highest exponent was obtained with lower level of binder and higher solid concentration as illustrated in [Fig. 17](#). This may be attributable to larger grain size which can reduce the clamp voltage ([Wu et al., 2008](#); [Roya et al., 2018](#)).

Energy absorption capability

Energy absorption capability of varistor made from powder with different binder systems is illustrated in [Fig. 18](#). There is no significant difference in the energy absorption capability among the varistors produced from the powder containing latex and the conventional binder, except a poorer performance was observed with binder Ltx C. The binder Ltx C showed enhance performance in terms of the powder characteristics ([Wu et al., 2008](#)) as well as electrical properties like watt-loss, clamp ratio, and nominal voltage etc., as mentioned before. The reason of poor performance in terms of energy absorption capability is not clear. The presence of lower and higher level of Ltx C at lower content of solid in the slurry resulted almost the same energy absorption capability as the conventional one as shown in [Fig. 19](#). However, it is much more consistent with Ltx C3 that is, at low level of Ltx C and high solid concentration as given in [Fig. 20](#). This consistency can be attributed to the presence of fewer flaws in the fired body as interpreted from Weibull modulus, m , for fired strength ([Begum and Hashmi, 2005a](#)). The failure mode is predominantly by electrical puncture for the varistor with all the binder systems.

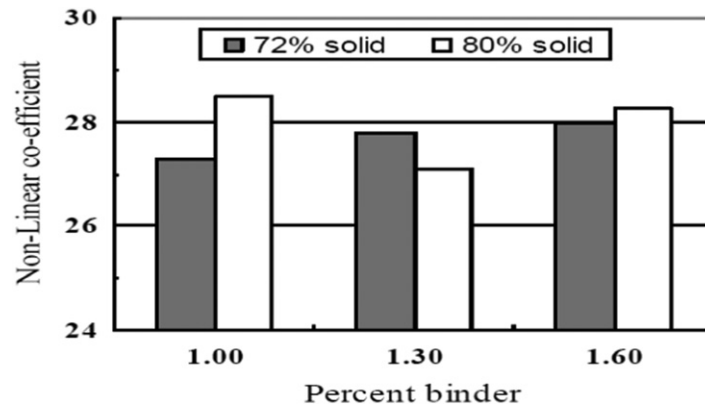


Fig. 17 Non-linear Coefficient of varistors with various levels of binder.

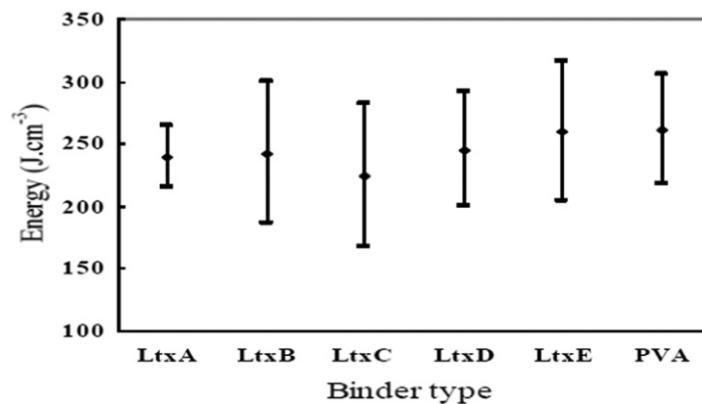


Fig. 18 Energy absorption capability of varistor disks with different binder systems.

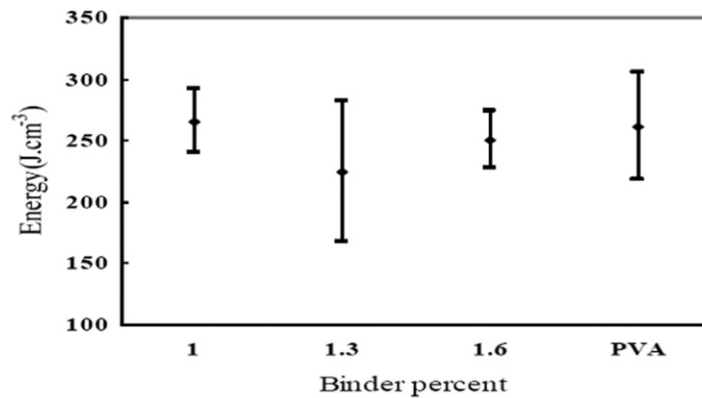


Fig. 19 Energy absorption capability of varistor disc with different levels of binder at 72% solid concentration.

Particle Size Analysis and Distribution of Particle Size

In fabricating ZnO varistor, the particle size and its distribution, the fraction percentage of each size influences significantly the particle arrangement and packing density, the size and the shape of the pore interstices, the deformation nature, sintering behavior and the microstructure developed during firing. The effect of the particle size distribution on sintering was observed by [Yeh and Sacks \(1988\)](#). They concluded that the green alumina compacts prepared from powders containing both narrow and wide size distribution can be sintered to high fired density without any exaggerated grain growth. However, the broad distribution will enhance the green density of compacts, and therefore, the shrinkage will be reduced to achieve the theoretical density. [Lange and Kellett \(1986\)](#) described the kinetics and transport theory for pore shrinkage with different packing arrangements and their

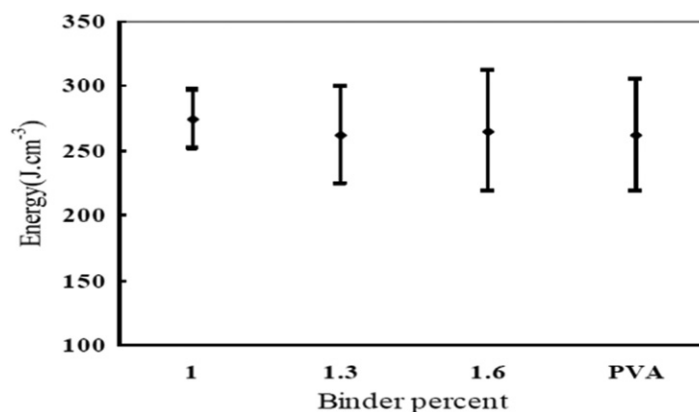


Fig. 20 Energy absorption capability of varistor disks with different levels of binder at 80% solid concentration.

dependence on the co-ordination number, ratio of the external surface energy to the grain boundary energy, short range and long range mass transport phenomena.

The significant influence of the particle size on the tensile stress of the compacts made of aluminum and copper powders are observed by German (1977), Duffield and Grootenhius (1959) concluded that for optimal strength the fine powder with narrow distribution is necessary. Rumpf's theory (Rumpf, 1962) explains the effect of the particle size and packing on the green strength of the compacts, the influence of flaws on the green strength, describes the variability of strength, and interprets the effect of powder mixing and of sintering environment. Nano-size ZnO and *core shell* type varistor powders were investigated by Pillai *et al.* (2003) and found that the *core shell* powder exhibited superior breakdown voltage than the commercial varistors. This breakdown voltage is greater than that of the samples prepared by simply mixing the nano-size ZnO and metal oxide powders.

Hingorani *et al.* (1993) have investigated ultrafine polycrystalline ZnO nanoparticles with size ranging from 5 to 40 nm and concluded that a higher critical electric field and a higher coefficient of nonlinearity (α) in the $\log(E)$ versus $\log(I)$ curve is achievable. Begum and Hashmi, (2005b) observed that spray drying yielded wide distribution of zinc oxide varistor powder. The percentage of fine and coarse particles in the granules can be varied by controlling spray drying parameters and the widely distributed powder resulted from higher feed flow rate and lower atomization pressure would increase percent of coarse granules in the powder which would lead to higher compressibility and enhanced green density. It was also observed by Begum *et al.* (2006) that the performance of varistor was also affected by percent of fine and coarse granules present in the spray dried powder. Though the nominal voltage was enhanced with higher percent of fine fractions, however, better energy absorption capability was achieved with increase fraction of coarse granules in the powder.

Sendi *et al.* (2014) observed that the solid state reaction is very much dependent on high surface area and the reduced particle size significantly influences the electrical properties, whereby, a sharp drop in the breakdown voltage is obtained and that has been found to strongly depend on grain size and potential barrier formation. Patent 20100136337 stated that ZnO varistor powder in which 50% of the particle diameter in the range of 20–120 μm can generates varistor with high operating voltage and excellent current-voltage nonlinear characteristics (Ando and Kasuga, 2010). Lanyi *et al.* (2007) concluded that ZnO varistor exhibited better electrical properties in terms of non-linear coefficient, breakdown voltage, leakage current and clamping voltage when prepared from powder produced by chemical synthesis (CS) than that of powder of mixed route. Zhu *et al.* investigated and found that intensive milling reduced the particle size of about 4 μm and enhanced the electrical performance significantly in terms of leakage current, breakdown voltage and non-linear coefficient (Roya *et al.*, 2018; Zhu *et al.*, 2012).

The standard spray dried ZnO varistor powder has particle size distribution within the range of 45–150 μm as presented in Fig. 21. The powder was fractionated to different narrow distributions containing large, medium and fine particles. A stack of sieves with 150, 90, 75 and 45 μm apertures was arranged successively from top to bottom. By placing the powder, the topmost sieve was closed with a lid and secured tightly. The sieves were agitated for about 30 min and the fraction of powder on each sieve was collected. The identification of different size fraction is given in Table 4.

Physical Characterization

The physical characteristics of disks prepared from the powder with narrow distribution of different size ranges and the standard one are shown in Table 5. The values within parenthesis are standard error. The green and the fired density did not show any appreciable difference but these are highest for cell D which had particle size smaller than 45 μm . The enhanced fired density was achieved as a result of higher capillary pressure exerted by the liquid formed during sintering. The total surface energy was also higher due to the small radius of curvature. Both the capillary pressure and surface energy provided more driving energy for densification.

The green strength was lowest with cell D, while it was almost the same for all the other cells including the standard one. According to Rumpf's theory (Rumpf, 1962) higher green strength was thought to be obtained from the powder containing smaller

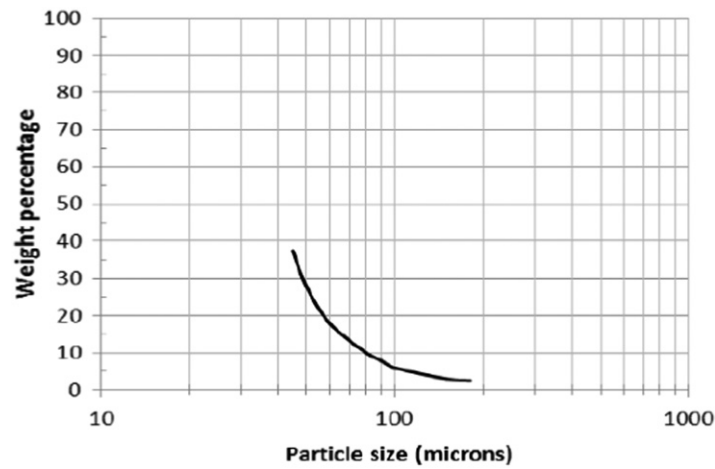


Fig. 21 Particle size distribution of standard ZnO varistor in production scale dryer.

Table 4 Identification of different size fractions of powder

Type of powder	Size range (μm)
Cell A	150–90
Cell B	90–75
Cell C	74–45
Cell D	<45
Standard powder	150–45

Table 5 Physical characteristics of disks produced from powder with different narrow size range

Powder type	Green density (gm/cc)	Fired density (gm/cc)	Green strength (MPa)
Cell A	$3.380 \pm (0.03)$	$5.60 \pm (0.011)$	$0.89 \pm (0.01)$
Cell B	$3.387 \pm (0.01)$	$5.60 \pm (0.014)$	$0.91 \pm (0.02)$
Cell C	$3.332 \pm (0.02)$	$5.58 \pm (0.028)$	$0.92 \pm (0.03)$
Cell D	$3.389 \pm (0.04)$	$5.62 \pm (0.015)$	$0.76 \pm (0.03)$
Standard	$3.334 \pm (0.03)$	$5.59 \pm (0.021)$	$0.91 \pm (0.03)$

particles. However, it is predicted that due to frictional effect the packing of the particles was not effective which reduced the strength.

Electrical Characteristics of Varistor With Different Size Fraction of Powder

The electrical properties were evaluated for the varistors fabricated from the powder of different size ranges including the standard distribution. The clamp ratio, non-linear coefficient (α), and watt-loss are summarized in [Table 6](#).

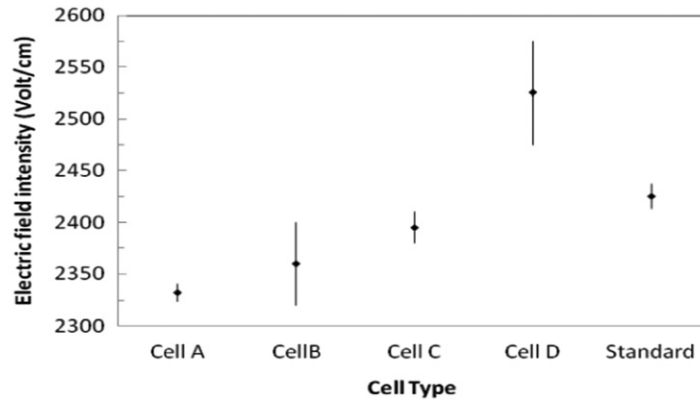
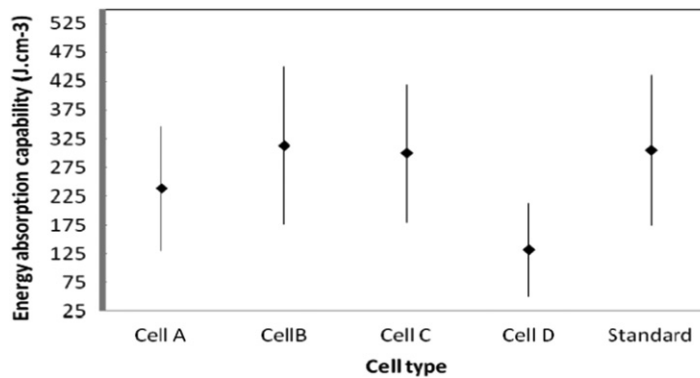
The clamp ratio and α did not change significantly for different cells. The clamp ratio was slightly higher and the non-linear coefficient was lower for cell D. The watt-loss before the application of the high amplitude short duration pulses of peak current 65 KA was found to be slightly higher for the same cell. But after the application of the high current pulses, increment in watt-loss was minimum for cell D making it comparable with varistors from all other cells.

Electrical Field Strength

This is also known as nominal voltage, threshold, turn on, or non-linear voltage and is used to rate a varistor. This corresponds to the voltage at which the flow of current from linear to non-linear mode starts. The nominal voltage of varistor produced from powder having different size ranges is plotted in [Fig. 22](#). The lowest was achieved for cell A and highest for cell D. The effect of particle size is clearly evident from the plot as cell A was composed of coarser particles and cell D of finer particles. It can be inferred that the coarser spray dried granules lead to bigger grains after sintering leading to lower nominal voltage. The finer granules generate smaller grains after firing.

Table 6 Clamp ratio, non-linear coefficient, and watt-loss for varistor fabricated with different size fractions of powder

Cell identification of varistors	Nonlinear coefficient (α) @ 1–5 mA	Clamp Ratio @ 5 mA-5KA	Watt-loss ($W\text{ cm}^{-3}$)		
			Before shot	After shot	
				Forward polarity	Reverse polarity
Cell A	15.041	1.693	0.010	0.011	0.013
Cell B	14.682	1.694	0.009	0.012	0.015
Cell C	14.498	1.692	0.009	0.011	0.013
Cell D	14.189	1.702	0.012	0.012	0.015
Standard	14.175	1.696	0.009	0.011	0.014

**Fig. 22** Electrical field strength of varistors produced from powders with different size fractions.**Fig. 23** Energy absorption capability of varistors produced from the powders with different size fractions.

Energy absorption capability

The energy absorption capability of the varistors was determined in Haefely (Model no. WO 4435–36, Hipotronics Inc., Brewster, New York) impulse generator with capacity of 50 KV and 45 KJ. The generator produces square wave which consist of LC network of capacitor and reactor coils in between capacitors.

Three repeated shots of 2 ms square wave were applied by selecting a charging voltage for a fixed charging time for each cycle. The energy absorption capability of varistors prepared from the powder containing particles of different size ranges is illustrated in Fig. 23. It is evident that the energy withstanding capability is low for cell D. The other fractions composed of coarse, medium and wide distribution of particles do not exhibit any noticeable difference. It can be said from the data presented in Table 4 that the green body is less homogenous for cell D. The inhomogeneity of the disks in the green state might be intensified further by firing. Hence the varistor failed at very low level of injected energy.

Conclusions

Application of acrylic latex polymer as binder in the processing of zinc oxide varistor has secured superior performance in terms of green and fired strength and electrical properties. The green properties of the varistor disks were improved with the use of new binder system. Significant improvement of green strength will facilitate the handling of green disc prior to sintering. Enhanced green properties were found to be translated into the fired strength and electrical performance of the disks. Higher nominal voltage, low watt-loss and clamp ratio, and consistency in energy absorption capability were secured with latex binder. But all the functional parameters were not found to be improved by the use of a single type of binder. The powder processed from the slurry containing lower level of binder and higher solid concentration could be a better choice in the context of several aspects. However, ultimate selection of a binder system could be made depending on the impact on the significant functional parameters identified on the basis of the type of application. The reliability of a surge protection system is largely dependent on the energy absorption capability of the arrester blocks being used. Disks having higher energy absorption capability are always desirable. Wide distribution of particles is desirable in varistor fabrication as it can enhance the overall performance.

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Beyond Li-Ion Batteries: Future of Sustainable Large Scale Energy Storage System

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Abstract

Since the first inception by Sony Co. in the year 1991, the Li-ion battery system is widely used in electronic devices, static energy depository systems, and electric vehicles (EVs) because of its high energy density compared to that of the existing systems, i.e., Lead-Acid, NiCd, NiMH. Due to the advent of new applications based on Li-ion battery systems, the secondary (rechargeable) battery market is expanding very rapidly. A higher energy density demand in the secondary battery system for some applications, especially for electric vehicles (EVs), has led researchers around the world to search for a battery system beyond Li-ion. Different “beyond Li-ion” battery chemistries are being examined as possible alternatives to Li-ion battery chemistries. This article particularly focuses on three “beyond Li-ion” battery chemistries: Li-S, Li-air, and Na-ion.

Key Points

- Shortcomings of the Li-ion battery (i.e., thermal runaway, internal short circuit) and its mitigation measures;
- The requirement of high specific energy battery system for some applications;
- Promising new alternative battery systems (beyond Li-ion).

Introduction

Secondary battery systems (rechargeable) that existed in the market (i.e., Lead-Acid, NiCd, NiMH) before the commercialization of Li-ion batteries (LIBs) had low energy density (Li *et al.*, 2018). The inception of the Li-ion battery by Sony Co. in 1991, which comes with the highest workable energy density, has changed the whole concept of possible application driven by the secondary battery system. Till today, they are considered one of the most propitious candidates for electric vehicles (EVs), cellular phones, and lap-top computers (Han *et al.*, 2015). Due to the high cost of Li-ion batteries and a finite driving range of EVs (specific energy of 80–120 Wh kg^{−1} correspond to a range of about 160–240 km), user accession of this battery system is relatively low (Seeba *et al.*, 2020; Thackeray *et al.*, 2012; Kurzweil, 2015). Though the technology of LIBs is enough mature, recently questions are being raised about safety issues, lifetime of LIBs, low-temperature performance, and cost of the batteries (Slater *et al.*, 2013). Maleki and Howard (2009) observed different Li-ion cells and the effect of design parameters on the performance during internal short circuit (ISC). They found that thermal runaway risk increases when the uncoated cathode (Al-current collector) section touches the anode. As a result, the thermal energy of the internal short circuit (ISC) can increase the local temperature up to 200°C (Maleki and Howard, 2009). Regarding gravimetric energy density, Li-ion battery could not satisfy the user. The future EV market needs a new battery system whose energy density is higher than the Li-ion battery, self-titled “beyond Li-ion battery”. Moreover, Li-ion battery uses non-aqueous electrolyte which is flammable. Therefore a questionable safety issue is always connected with the use of Li-ion battery (Luntz, 2015). Alternative battery systems such as Li-air, Li-S, Zn-air, Mg-ion, Na-ion, etc., have the potentials to replace the traditional Li-ion battery.

Intense research on non-aqueous Li-S and Li-air batteries are conducted recently because of their higher energy density (Luntz and McCloskey, 2014; Manthiram *et al.*, 2014). Li-air battery shows a high achievable energy density and it is an open system where cathode active material is not stored. This Li-air battery consists of an anode (pure Li-metal) and porous cathode (carbon) separated by a membrane (hybrid design) and an electrolyte (aqueous, aprotic, or solid) and uses oxidation of lithium at the anode and reduction of oxygen at the cathode to induce a current flow. Because of having an open system, Li-air battery exhibits higher specific energy in comparison with Li-ion batteries. The specific energy achievable by Li-air battery chemistry is around 1.0 kW h Kg^{−1} (Sapunkov *et al.*, 2015; Christensen *et al.*, 2012). Li-S battery is also a very attractive choice in terms of its intrinsic high energy content (five times than the Li-ion battery), excellent power capability, and low cost. The unique characteristic of the Li-S batteries is to provide intrinsic overcharge protection, and thus, the safety of the battery is enhanced (Amine *et al.*, 2014). Na-ion batteries can also be considered a promising alternative to LIBs. The low material cost and abundance of sodium make the Na-ion batteries attractive over LIBs (Slater *et al.*, 2013). At low-lying operational voltage, Na does not make any alloy forming reaction with aluminum (Al). Therefore, aluminum foils are being used as current collector for both the electrodes in Na-ion batteries.

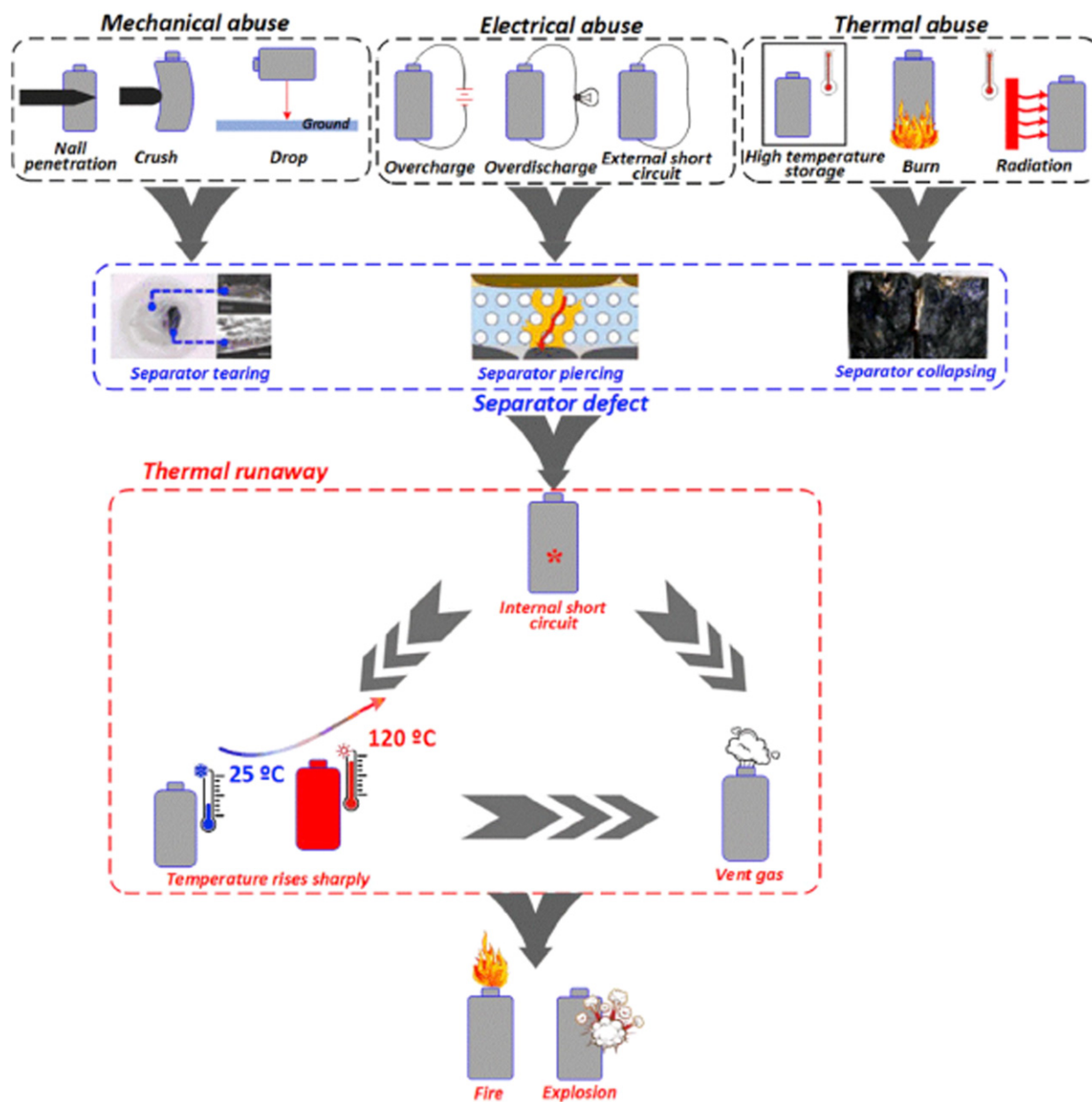


Fig. 1 Schematic diagram on thermal runaway mechanisms inside the Li-ion batteries. Reproduced from Liao, Z., *et al.*, 2019. A survey of methods for monitoring and detecting thermal runaway of lithium-ion batteries. *Journal of Power Sources* 436, 226879. Available at: <https://doi.org/10.1016/j.jpowsour.2019.226879>.

Thus, copper current collector can be replaced by Al. The material cost of the Na-ion battery is low because high-cost Li, Cu and Co are not used and Na itself is about half the cost of Li. The stability of Na-ion batteries is magnified due to Na-ion's lower operational voltage (Kubota *et al.*, 2018; Massé *et al.*, 2015).

The shortcomings of rechargeable Li-ion batteries and their possible solutions are discussed in the following sub-sections. Besides, some alternative battery chemistries to traditional Li-ion battery systems are also highlighted.

Shortcomings of Li-Ion Battery

Thermal Runaway

Many electrochemical side reactions occur inside the Li-ion batteries which give rise to exothermic reactions. The conditions that cause the thermal runaway (i.e., mechanical, electrical, and thermal abuse) leads the temperature inside the battery to increase very sharply

Table 1 Reactions responsible for heat generation and their starting temperature

Reaction	Heat generation	Starting temperature (°C)
Decomposition of SEI	$Q_{\text{sei}} = H_{\text{sei}}W_cR_{\text{sei}}$	90–120
Reaction of Negative Solvent	$Q_{\text{ne}} = H_{\text{ne}}W_cR_{\text{ne}}$	120
Reaction of Positive Solvent	$Q_{\text{pe}} = H_{\text{pe}}W_pR_{\text{pe}}$	170
Electrolyte Decomposition	$Q_e = H_eW_eR_e$	>200

Note: Parhizi, M., Ahmed, M.B., Jain, A., 2017. Determination of the core temperature of a Li-ion cell during thermal runaway. *Journal of Power Sources* 370, 27–35. Available at: <https://doi.org/10.1016/j.jpowsour.2017.09.086>. Kim, G.-H., Pesaran, A., Spotnitz, R., 2007. A three-dimensional thermal abuse model for lithium-ion cells. *Journal of Power Sources* 170 (2), 476–489. Available at: <https://doi.org/10.1016/j.jpowsour.2007.04.018>. Roth, E.P., Doughty, D.H., Franklin, J., 2004. DSC investigation of exothermic reactions occurring at elevated temperatures in lithium-ion anodes containing PVDF-based binders. *Journal of Power Sources* 134 (2), 222–234. Available at: <https://doi.org/10.1016/j.jpowsour.2004.03.074>.

due to the exothermic chain reactions that damage the internal structure and thus degrades its performance. The thermal runaway mechanism of Li-ion batteries under various conditions is illustrated in Fig. 1. Thermal runaway, as well as following propagation of thermal runaway, are behind the catastrophic failure of Li-ion batteries. The battery safety mechanism can be understood by examining the propagation of thermal runaway. There are two principal propagation modes, increment of overall temperature and localized superheating, that cause the mode of propagation. Jia *et al.* (2020) stated five stages of thermal propagation – (1) firstly, the battery gets short-circuited, (2) runaway reaction inside the first battery of the pack is then started, (3) neighboring batteries get heated by the flame caused by the first battery, (4) second battery of the pack is short-circuited due to overheating of the local area, and (5) runaway reaction inside the second battery causes many gas blasts (Jia *et al.*, 2020). Lopez *et al.* (2015b) explained the thermal runaway (TR) by successive distinguished events such as rampant temperature spikes followed by fire, smoke, cell venting, and an explosion of battery contents.

Thermal runaway is one of the main causes of fire and explosion in Li-ion batteries. The release of flammable gases during thermal runaway side reactions builds concentrated pressure inside the battery and may cause rupture of the cell case. Any sort of ignition may lead to fire as well as explosion due to the presence of these flammable and toxic gases. Yuan *et al.* (2020) performed a gas chromatograph (GC) to analyze the concentration of gases vented from batteries with different chemistry. They reported, LFP (iron phosphate cathode) cells generated a higher amount of H_2 , C_2H_2 , C_2H_4 , and C_2H_6 , but a lower amount of CO. The NMC (nickel manganese cobalt cathode) cell generated minimum C_2H_4 and C_2H_6 , but a very high amount of CH_2 and CH_4 . The LTO (titanate anode) cell generated a very high amount of CO_2 and minimum H_2 , CH_4 , and C_2H_2 . Flammable gases like H_2 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , CO, HF, POF_3 , PF_5 , ethyl fluoride, propylene, etc. can produce fire as well as explosion when mix with oxygen and create a flammable air/fuel ratio (Yuan *et al.*, 2020; Hammami *et al.*, 2003; Sun *et al.*, 2016). The total amount of heat generated at the time of thermal runaway is the summation of heat produced from multiple sources like decomposition of the solid-electrolyte interface (SEI), the reaction of negative solvent, the reaction of positive solvent, and decomposition of the electrolyte. All the above reactions individually initiate at a definite temperature (Kim *et al.*, 2007). Table 1 shows the reactions responsible for heat generation and their initiation temperature.

The total amount of heat generated within the cell during thermal runaway can be calculated using the following equation:

$$Q_{\text{gen}} = Q_{\text{sei}} + Q_{\text{ne}} + Q_{\text{pe}} + Q_e \quad (1)$$

Parhizi *et al.* (2017) in their work computed core temperature and the reported surface temperature of $LiCoO_2$ 18,650 cell undergoing thermal runaway, as shown in Fig. 2. It is evident that for the first 600 s, the cell's surface temperature is higher than its core temperature. This happens as the initial cell temperature is lower than the oven, and at the initial stage, insignificant heat is generated from the chemical reactions. At this stage, core temperature is raised due to heat diffusion from surface to core. When the temperature of the cell rises significantly, a large amount of heat is generated from chemical reactions. Therefore, the slope of the temperature curve is very sharp. The temperature peak at the core is several hundreds of °C greater compared with the surface. After the completion of thermal runaway, heat is diffused to the surface from the core. The temperature of the core remains higher till the core and surface equilibrate at oven temperature (Lopez *et al.*, 2015a; Parhizi *et al.*, 2017). Overcharging can lead to thermal runaway. Overcharge is caused due to failure of the charger or malfunction of the charger. It is important to learn about the behavior of heat generation because thermal runaway is intimately related to a cell's temperature rise. Heat flow rises at the time of overcharging as the voltage is kept at nearly 4.2 V. Generated heat decreases quickly when the charging is terminated. The cell voltage quickly decreases nearly 1.5–3.5 V below the charging voltage. These phenomena point out that the batteries deteriorate due to overcharging. From the tie-up between charging current and heat flow, during overcharging, heat flow is nearly in proportion with the current. A proper cooling system can eliminate the possibility of thermal runaway generating from overcharging (Saito *et al.*, 2001).

Protections against the thermal runaway

Putting a stop to the consequences originated by the thermal runaway (TR) in Li-ion batteries, it is necessary to take preventive steps against thermal runaway. Two-step mechanisms can be employed to limit or reduce the thermal runaway: (1) upgrading the intrinsic safety issues of Li-ion batteries, and (2) enabling cooling capability at module or pack level. The heat dissipation technique can cool down the Li-ion batteries using liquid, forced air, and phase-changing materials. Thus, the severity of thermal runaway can be minimized. Isolating the heat propagation is a good initiative to prevent thermal runaway mechanisms by blocking the path of heat

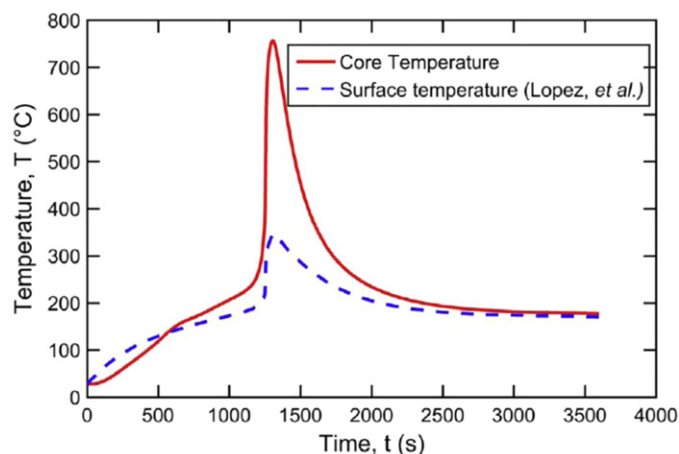


Fig. 2 Computed core temperature compared to the reported surface temperature at a certain time zone (LiCoO₂ 18,650 cell measured in a traditional oven test. Reproduced from Parhizi, M., Ahmed, M.B., Jain, A., 2017. Determination of the core temperature of a Li-ion cell during thermal runaway. *Journal of Power Sources* 370, 27–35. Available at: <https://doi.org/10.1016/j.jpowsour.2017.09.086>.

transfer between a healthy and damaged battery. As a result, the chain reactions can be stopped and so do the thermal runaway (Liao *et al.*, 2019). Safety issues associated with thermal runaway mechanisms include both chemistry and material science & engineering which are very complex to address at a time. Using different types of electrolytes, electrode materials, and cells exhibit diverse thermal runaway behaviors that are unlike each other. Electrochemical reactions at different stages of thermal runaway depend on materials of component, cathode, electrolyte, and anode. The intrinsic safety method is the main and final way for solving the thermal runaway problem. Battery explosion can be prevented by coupling with intrinsic safety methods through the usage of safety devices (Wang *et al.*, 2012; Feng *et al.*, 2020a). Mohammadian and Zhang (2018) studied the influences of implanted microchannels on the wettability of electrodes as well as their effectiveness in preventing thermal runaway. They found that the chemical reactions responsible for thermal runaway are: (1) decomposition of SEI, (2) reaction between the electrolyte and negative active-material, (3) reaction between electrolyte and positive active-material, (4) decomposition of electrolyte, and (5) reaction between negative-active material and binder. More than one of the above-mentioned reactions can occur at the same time. Jumping the cell into a higher reaction level can be prevented by venting the gases generated during thermal runaway. For instance, if the generated hydrocarbon gases are vented out of the cell, internal pressure and temperature will not rise. Thus, cathode material will not break down and no oxygen will generate. Implanted microchannels in the electrode can vent the gases which are generated from exothermal reactions. Thus, the microchannels prevent the cells' thermal runaway (Mohammadian and Zhang, 2018).

Internal Short Circuit (ISC)

Four major types of short circuit occur in Li-ion batteries, and these are: (1) short between copper and aluminum current collector, (2) short between Cu current collector and cathode material, (3) short between Al current collector and anode active material, and (4) short between both the active material (anode and cathode). The internal short circuit (ISC) process is very swift and this process is controlled by the reactants' behavior at the local area of short initiation (Santhanagopalan and Ramadass, 2009).

A short circuit does not only occur from the fracture of the separator, but also due to the fracture of a jelly roll. Greve and Fehrenbach (2012) performed a mechanical test on cylindrical Li-ion cell (GAIA, HP 602030 NCA-45 Ah/162 Wh). They reported that the cell can tolerate a significant amount of deformation before an internal short circuit. However, just before the internal short circuit (ISC) initiation, they noticed a sudden decrease in applied force level in some of the curves (i.e., load-displacement curves). They assumed, due to a structural fracture in the jelly roll, the load was dropped. Jelly roll fracture helps in relative motions of the unprotected anode and cathode material. Due to this relative movement, direct contact between anode and cathode occurs which leads to the initiation of ISC (Greve and Fehrenbach, 2012; Xiong *et al.*, 2020). The development of ISC in Li-ion batteries under mechanical loading is rather a complex phenomenon. Sahraei *et al.* (2016) developed a micromechanical replica to know the failure sequence in multi-layer and multi material structure of jelly roll. They put in three distinct amalgamations of tensile and compressive deformations on the representative volume elements (RVE). In the first trial, they applied an equal amount of tension and compression load. Then, the value of compression loading was increased twice to that of tension. And, finally, tension loading was twice the compression. When compression loading was equal to or twice than the tension, the aluminum foil failed before the electrolyte separator. But, when the tension loading was twice than the compression, the aluminum foil failed at first, then the copper foil, and lastly the electrolyte separator. The compressive/tensile strain ratio versus the tensile strain which is responsible for separator failure is shown in Fig. 3. Electrolyte separator failure is the manifestation of an impending short circuit (Sahraei *et al.*, 2016).

Love *et al.* (2014) studied the growth of Li-dendrite by examining the dendrite number, time of initiation, and rate of growth at ambient as well as sub-ambient temperature (−10°C, 5°C, and 20°C). They used an in-situ optical microscope for the experiment.

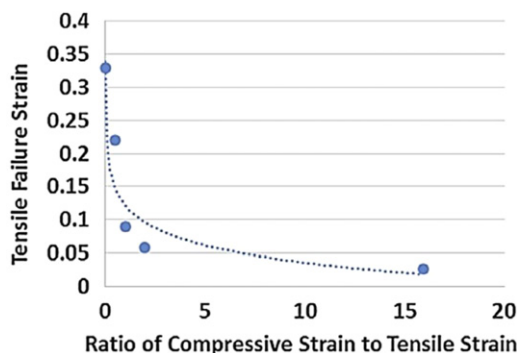


Fig. 3 Compressive strain/tensile strain versus tensile strain to failure. Reproduced from Sahraei, E., *et al.*, 2016. Microscale failure mechanisms leading to internal short circuit in Li-ion batteries under complex loading scenarios. *Journal of Power Sources* 319, 56–65. Available at: <https://doi.org/10.1016/j.jpowsour.2016.04.005>.

While charging, the formation of Li-dendrite at the anode can lead to an internal short circuit (ISC). At low temperatures, dendrite grows at a faster rate because of increased resistance to mass transport of Li-ion across the viscous electrolyte and lessened resistance to charge transfer generated by SEI (solid electrolyte interface). The growth rate of needle shape dendrites with a large aspect ratio is higher than the blunt round shape dendrites. The time of ISC, t_{SC} , can be calculated from Eq. 2.

$$t_{sc} = t_i f(T) + l/v_d f(i, T, \text{morphology}) + \text{morphology } f(T) \quad (2)$$

Here, l = Electrodes distance

i = Applied current

T = Temperature

Cell shorting occurs when the dendrites create a pathway between the negative and positive electrode (Love *et al.*, 2014). Factors like the formation of bubbles during charging and discharging can also affect the dendrite evolution. The gap between the electrodes is filled by dendrite. A large amount of current flows across the cell when the dendrites interconnect the electrodes. The flow of this current melts the dendrites and disconnects them from the cathode. As a consequence of dendrite melting, Li-ions are attracted by the small dendrites at the interface (electrode/electrolyte). As a result, these small dendrites at the interface grow up. If the cell charging reaction is continued, the fragmented dendrites will reconnect with both electrodes. This bridging, as well as ablation phenomena, will iterate till the electrodes' gap is filled by dendrites (Zhu *et al.*, 2019).

Mitigation of ISC

Mechanical strength of the current collectors in the Li-ion cell is higher than the active material layer used in the electrodes, thus, cracking of the current collector dominates the electrode fracture. A metallic thin film undergoes radial cracking (petaling) when dynamic loading is applied. If the electrodes' petals are compressed together, an internal short circuit is formed and the current collector provides a conductive pathway. If circumferential cracking is promoted instead of radial cracking by generating proper surface notches, it will help to separate the petals from shorting. Surface notches' geometry influence the crack propagation mode within the modified current collector. Surface notches with triangular as well as hexagonal patterns show the tendency of radial cracking. But, the double-curved edges square shows the tendency of circumferential cracking (Wang *et al.*, 2017a,b). Wang *et al.* (2017a,b) discussed functional current collector (FCC) for mitigation of internal short circuit of high voltage Li-ion batteries. A functional current collector (FCC) can be produced by debossing the flat current collector to form a square shape double-edged web of surface grooves. These grooves concentrate the stress and alter the allocation of stress. When the strain reaches the failure strain, cracks initiate at the root of the surface grooves and tend to propagate alongside the surface grooves. As the cracks bifurcate alongside the double-edged routs, transverse cracks disintegrate the petals within the radial cracks. The fracture of the membrane separator exactly follows this similar pattern. Due to the formation of fracture, the effective shorting resistance can be increased by more than one order of magnitude (Wang *et al.*, 2017a,b). As we know the formation of Li-dendrites is mainly responsible for ISC and this dendrite initiation time is rapid at lower temperature range (i.e., -10°C and 5°C) and slower at a temperature around 20° (Love *et al.*, 2014). Therefore, mitigation measures such as avoiding charging at low temperatures can effectively prevent the rapid initiation and growth of the Li-dendrites.

Beyond Li-Ion Battery

With the need for high energy density and better safety to meet the demand for future uses such as long-range EVs, the industry is looking for new materials and other chemistries (Amine *et al.*, 2014). Researchers all over the world have been so far focusing on three avenues: (1) multivalent chemistries, (2) solid-state batteries, and (3) other battery systems (e.g., conversion cathodes such as metal/Sulfuring, metal/air, Na-ion, etc.). Here, only three such battery systems (i.e., Li-S, Li-air, and Na-ion batteries) with high potential to meet the future demand for automotive and stationary storage applications are discussed in the following sections.

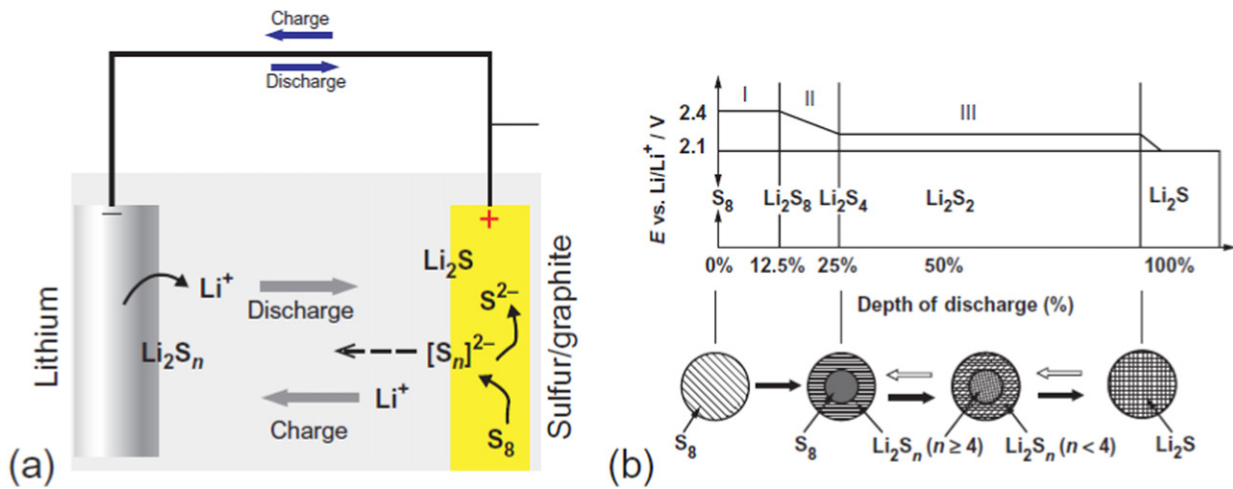
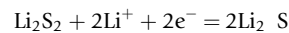
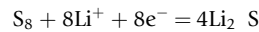


Fig. 4 Lithium-sulfur battery: (a) cell design and electrode reactions, (b) stages during discharge. Reproduced from Kurzweil, P., 2015. Post-lithium-ion battery chemistries for hybrid electric vehicles and battery electric vehicles. In: Scrosati, B., Garche, J., Tillmetz, W. (Eds.), *Advances in Battery Technologies for Electric Vehicles*. Elsevier. pp. 127–172.

Rechargeable Li-S Batteries and Key Challenges

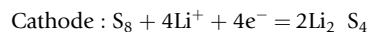
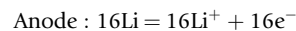
In Li-ion batteries, the cathode materials that are used are mainly compound materials that limit the charge storage capacity as well as the energy density of the batteries. Due to the rapid surge in the demand for EVs as well as portable electronics, a new energy storage system is required with high efficiency and energy density. Because of their large theoretical energy density ($\sim 2567 \text{ Wh kg}^{-1}$) (Sawas *et al.*, 2019) and high theoretical specific capacity (1675 mAh g^{-1}) (Feng *et al.*, 2020b), Li-S rechargeable batteries are thought of as one of the promising contenders for new generation energy storage devices used in electric vehicles (EVs) and electric grids.

Typical Li-Sulfur batteries are made up of a cathode (composite of sulfur), anode (Li-metal), and organic electrolyte (See Fig. 4(a)). At the time of discharge, at first, higher-order Li-polysulfides Li_2S_x ($4 \leq X \leq 8$) are formed, and then lower-order Li-polysulfides Li_2S_x ($1 \leq X < 4$) (See Fig. 4(b)). At the time of charging, elemental S is formed through the generation of intermediate Li-polysulfides due to oxidation of Li_2S (Yan *et al.*, 2019; Zhang and Guo, 2019). The cathode of this kind of battery is mainly made of microporous carbon. They considered the elementary sulfur in S_8 form, which is sequentially reduced into Li_2S_2 and Li_2S .

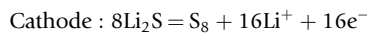
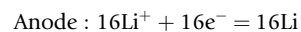


The formation of Li_2S_2 and Li_2S is a two-phase chemical reaction because sulfur lithiation goes as a layer by layer mechanisms. Due to the insulating characteristics of S_8 and Li_2S_2 , electron transfer may depend on the electron tunneling (Yin and Franco, 2018). The reactions associated with discharging and charging are (Yang *et al.*, 2018):

Reactions during discharging



Reactions during charging



Li-dendrites formation and polysulfides shuttling are two considerable obstacles faced in the advancement of Li-S batteries. The shuttling effect is raised due to the dissolution of long-chain Li-polysulfides into the electrolyte. C-S structure with a short sulfur chain is being used to combat the shuttling effect. Xu *et al.* (2020) suggested the use of a hybrid electrolyte, made of SSE (sulfide solid electrolyte) and LE (liquid electrolyte), that are found to reduce these obstacles. SSE acts like a barrier to mitigate polysulfide shuttling as well as Li-dendrites growth. LE helps in the rapid transportation of Li^+ . The traditional polymer separators are not good enough to provide a physical barrier to polysulfides. Li-S batteries with hybrid electrolytes can work at a high charge and discharge rate, i.e., at 5C (7.10 mA cm^{-2} or 12.532 mA) discharge capacity was found to be 659.4 mAh g^{-1} at the initial stage. After 50 cycles and 100 cycles, the discharge capacity is maintained at 471.4 mAh g^{-1} and 413.3 mAh g^{-1} , respectively. Capacity retention is therefore 71.53% and 62.67% (Xu *et al.*, 2020). The retainment of polysulfides at the cathode is another challenge in the Li-S battery system. The addition of additives in the cathode matrix is found to captivate the polysulfides and prevent them to diffuse from the cathode to anode. Evers and Nazar (2013) explored mesoporous silica as an additive to a large pore mesoporous carbon/sulfur electrode and found it effective to contain polysulfide by interacting through surface-sorption, and subsequently

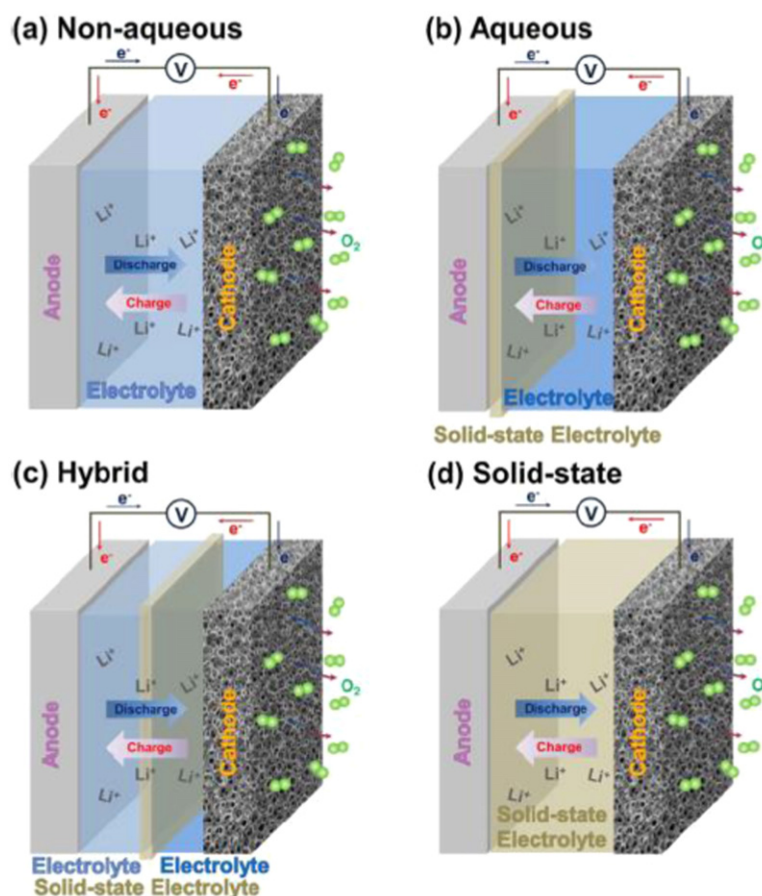


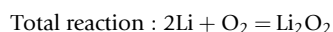
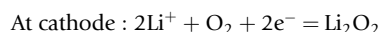
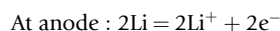
Fig. 5 Schematic layout of Li-air batteries. Reproduced from Tan, P., *et al.*, 2017. Advances and challenges in lithium-air batteries. *Applied Energy* 204, 780–806. Available at: <https://doi.org/10.1016/j.apenergy.2017.07.054>.

decrease their concentration in the electrolyte and leading to higher utilization of sulfur and increased capacities (Evers and Nazar, 2013). For combating the growth of Li-dendrites, a polydopamine (PD) coated separator is used. Another attempt to suppressing dendrite growth is the addition of CsNO_3 into the electrolyte. When Cs ions are added at a controlled amount, they can stay at cationic state surprisingly at a voltage at which Li^+ becomes Li° . Cs ions inhibit the deposition of Li-metal above Li-metal surface at morphological spots. Thus, the growth of dendrites is suppressed. NO_3^- ions help in the formation of a strong interfacial layer at the surface of Li-metal in Li-S batteries (Kim *et al.*, 2014; Ding *et al.*, 2013; Xu *et al.*, 2013; Gaissmaier *et al.*, 2019).

Rechargeable Li-Air Batteries and Key Challenges

Li-air batteries, having high theoretical energy density, are one of the promising options to replace the typical Li-ion batteries. Li-air batteries can be classified into four types based on the electrolytes used: non-aqueous Li-air batteries, aqueous Li-air batteries, hybrid Li-air batteries, and solid-state Li-air batteries (Fig. 5). The specific energy density of non-aqueous and aqueous Li-air batteries is found to be 3460 Wh kg^{-1} and 1910 Wh kg^{-1} , respectively (Imanishi and Yamamoto, 2014). Because of possessing high specific energy density, non-aqueous Li-air batteries are widely studied (Lee *et al.*, 2011; Lyu *et al.*, 2017). To compare with a typical Li-ion battery system, the specific energy density of non-aqueous Li-air batteries is almost 10-fold higher (Imanishi and Yamamoto, 2014). Non-aqueous Li-air battery consists of a cathode, Li-anode, separator, and electrolyte. The cathode of Li-air batteries is exposed to air. The operating mechanism of Li-air batteries is dissimilar to the LIBs. Li-air batteries use O_2 from the ambient air to store and convert energy. During discharging Li-metals are converted into Li^+ and move to cathode. Meanwhile, a discharge product is formed at the cathode. Li_2O_2 is the principal discharge product of Li-air batteries.

Electrochemical reactions of Li-air batteries:



However, the research history of Li-air batteries is very young and it is still in the development stage. Shortcomings like poor energy efficiency, small cycle life, and low rate capability are associated with Li-air batteries (Wang *et al.*, 2019; Aurbach *et al.*, 2016; Zhang *et al.*, 2018; Song *et al.*, 2017). High energy Li-air (non-aqueous) battery can be prepared by overcoming product resistivity. Morphology, as well as conductivity of discharged products produced in Li-air batteries, perform a great role in developing high capacity non-aqueous Li-air batteries.

Growth mechanisms of Li_2O_2 and particle morphology in Li-air batteries are still obscure. Cell capacity decreases due to electron transfer through lithium peroxide (Li_2O_2) deposit. Pure lithium peroxide behaves like an insulator. Deposition of Li_2O_2 during discharging can strangle the flow of current. Loss of capacity with current is considered a major problem for obtaining large power-density as well as large gravimetric energy-density at a time (Girishkumar *et al.*, 2010). The use of additives and solubilizing electrolyte-solvent may mitigate the problems associated with product resistivity. The use of novel electrodes offers a high pore volume. Poor blockage can be avoided by using the correct pore structure. A mixture of non-wetting and wetting pores ensures an excellent transportation rate of Li-ion and O_2 at the reaction area during discharge (Christensen *et al.*, 2011). Li-metal anodes are used in Li-air batteries because of the high energy density of Li-metal, however, dendrite formation and electrolyte incompatibility are associated with Li-metal. Dendrite formation can lead to an internal short circuit. As a solution to prevent this dendrite formation, anodes (Li-metal) with a protective coating can be used to separate the Li-metal anodes from electrolytes. The promising coating materials are Li-ion conductive polymers, glasses, and ceramics. Besides, the liquid electrolyte can be replaced by a solid polymer-electrolyte. Polymer electrolytes can be divided into three types based on the applied materials: (1) gel polymer (polymer network with liquid electrolytes), (2) solid polymer (polymer-salt complex), and (3) composite polymer (inorganic fillers into the organic polymer host). These polymer-electrolytes can conduct Li^+ but inert to Li-metal, and also able to prevent dendrite formation (Kraytsberg and Ein-Eli, 2011). The reactions that occur at the Li-anode/electrolyte interface in non-aqueous Li-air batteries are complicated. Passivation film and suitable membrane can be used to protect the Li-electrode (Tan *et al.*, 2017).

The constituents of air (N_2 , CO_2 , and H_2O) affect the oxygen electrochemistry in Li-air batteries. CO_2 contamination in Li-air batteries degrades the electrolyte because of Li_2CO_3 formation. Removal of Li_2CO_3 degrades the electrolyte and electrode. Li_2CO_3 decomposes at high potential (> 4.0 V versus Li/Li^+), and as a result, Coulombic efficiency and cycle life are reduced. Therefore, the formation of Li_2CO_3 in Li-air batteries should be avoided (Liu *et al.*, 2020; Imanishi and Yamamoto, 2019). Most of these chemical reactions are side reactions that are induced by carbon instability in non-aqueous electrolytes. Both nanostructured porous carbon cathodes and carbon-free cathodes are being investigated extensively to improve the stability and reversibility of the cathode, thus, cycle life, as well as round trip efficiency, can be enhanced (Jung *et al.*, 2016).

Rechargeable Na-ion Batteries and Key Challenges

Na-ion batteries (SIBs) are another promising new electrochemical energy storage system and attract much attention recently. They are one of the strong alternative options to be considered for replacing Li-ion batteries because of their high energy density, better cycle life, and better cycling stability (Chayambuka *et al.*, 2018; Hwang *et al.*, 2017). Moreover, this Na-ion battery technology is a greener and sustainable battery system. Thus, it can be one of the ways to electrify the entire world without producing an environmental burden (Tarascon, 2020). One salient safety advantage of Na-ion batteries over typical Li-ion batteries is that they can be stored or transported at an empty energy state (0 V). One physical short circuit is present in between two tabs (positive and negative). On the contrary, it is necessary to transport the Li-ion batteries at a defined charge state (30%) to prevent the dissolution of the copper current collector. This transportation condition presents a safety risk for air transportation of Li-ion batteries (Bauer *et al.*, 2018). Anode and cathode materials of Na-ion batteries can be classified into four groups; for anodes: (a) carbonaceous, (b) alloy, (c) phosphoric, and (d) sulfides or metal oxides, and for cathodes: (1) layered O_3 , (2) layered P_2 , (3) polyanionic compounds, and (d) Prussian blue analogs (PBAs) (Roberts and Kendrick, 2018). Luo *et al.* (2016) in their study found hard carbon as a promising candidate for anode materials for the vast production of Na-ion batteries (Luo *et al.*, 2016). The high-capacity alloying anodes have the potential to show better performance in near future and there is room for further research in this area. Palomares *et al.* (2012) examined phosphate-based cathode materials (i.e., NaFePO_4 , NaVPO_4F , $\text{Na}_2\text{FePO}_4\text{F}$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$) in Na-ion batteries and found it a suitable candidate. Because of the inductive effect, phosphates exhibit high voltage and thermal stability. For better electrochemical performance these phosphates need conductive coating (Palomares *et al.*, 2012). Ji *et al.* (2020) reported about the use of redox shuttle to protect the SIBs from overcharging. They developed a new redox shuttle called trisaminocyclopropenium perchlorate (TAC.ClO_4). TAC.ClO_4 exhibits some good merits like rapid diffusion rate, high solubility, and high solubility in redox states. Due to TAC addition, heat generation in overcharged cathodes reduced by 20% (Ji *et al.*, 2020). Zhou *et al.* (2019) designed a self-chargeable Na-ion battery (SCNIB) where a perforated piezo separator was used. This energy device exhibits good cycling stability, energy density, high flexibility, and better self-charging performance. This type of battery can charge itself up to 0.65 V by 150 s random bending or 300 s palm patting by accumulating mechanical energy. Some common electronic devices can be powered by serially connecting SCNIBs (Zhou *et al.*, 2019).

Concluding Remarks and Perspectives

The gaining popularity of higher-efficiency electric vehicles (EVs) over the low-efficiency internal-combustion-engine vehicles (ICEV) pulls the demand to develop a stable, safe, environmentally friendly new battery chemistry that has the potential for higher

energy densities than the Li-ion, so-called “beyond Li-ion”. Moreover, the integration of renewable energy sources into the electric grid requires safe and reliable extensive electrochemical energy storage. To encounter the challenges faced in “beyond Li-ion” systems, a combination of chemistry, electrochemistry, physics, engineering, and manufacturing is necessary. In this article, three high-potential battery systems (i.e., Li-S, Li-air, and Na-ion batteries) have been highlighted and discussed. Along with many other alternatives, these three battery systems offer attractive prospects as a future electric power source and are believed to meet the future high specific energy and safety requirements for automotive and stationary storage applications. The endeavor to search for new materials, as well as mechanisms, is necessary to continue to combat the challenges encountered (e.g., dendrite formation, electrolyte breakdown, and electrode instability) with such battery systems.

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Automated EELS Core-Loss Edge Detection for Quantification of the Chemical Composition of Nano-Structured Semiconductors

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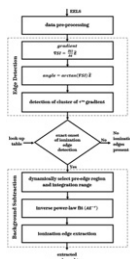
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Abstract

Two automated algorithms for the detection of ionization core-loss edge onsets are proposed. The first algorithm uses a look-up table to identify the core-losses by identifying positive slope-angle clusters. The second algorithm uses standard peak detection algorithms to detect the signals formed on top of an exponentially decreasing background at each point of the spectrum image. The limits of the ionization edge identification algorithm by peak detection is tested by choosing different window lengths, specimen thicknesses, additive white noise and effects of spectra smoothing using an averaging filter.

Graphical Abstract



Graphical representation of treating osteochondral defects using tissue engineering.

Highlights

- The objective of this article is to automate the quantitative analysis of electron energy-loss spectra by automatically detecting the ionization core-loss edges.
- Proposal of two automated ionization core-loss edge onset detection algorithms. First algorithm uses look-up table to identify the core-losses by counting positive slope-angle clusters. The second algorithm uses the standard peak detection algorithms to detect the peaks formed by the exponent of the background at each point of the spectrum.
- The limits of the edge detection algorithm by peak detection is tested by choosing different window lengths, specimen thickness, additive white noise and effects of smoothing using an averaging filter.

Introduction

Electron energy-loss spectroscopy (EELS) is ideal for quantification of the elements present in a material at near atomic resolution (Reimer, 1995). The amount of kinetic energy that is lost by an incident electron to excite an electron inelastically from an inner atomic shell is the cause for the formation of core-loss edges (Egerton, 2011). The intensity of core-loss edges of an element in EELS is via the ionization cross-section related to the number of atoms of that element. The minimum incident energy of an electron required to ionize an electron from a particular shell produces the ionization edge onset for that shell. However, any excessive incident energy can also cause the ionization where the electron still retains excessive kinetic energy. In energy-dispersive X-ray spectroscopy (EDXS), the transitions are the difference between two ionization shells and detected X-rays are of discrete energies. Hence in EDXS, the ionization signals are peaks while in EELS they are ionization edges with an exponential decay after the onset. The EEL spectrometer sorts the scattered electrons according to their kinetic energy. Some of the standard imaging techniques used in acquisition of EELS are shown in Fig. 1. The most common system is a TEM fitted with a magnetic prism. The beam entering the prism contains elastically and inelastically scattered electrons whose energy-loss occurred in the specimen. The magnetic prism is used to sort the electrons according to their kinetic energies and the electrons are collected by a spectrometer at 90° to the optical axis. The instrumental arrangement is shown in Fig. 1(a). An alternative setting is to arrange the spectrometer to be in the TEM column. To get the imaging stability there are multiple prisms that bend the beam in the shape of an Omega (Ω).

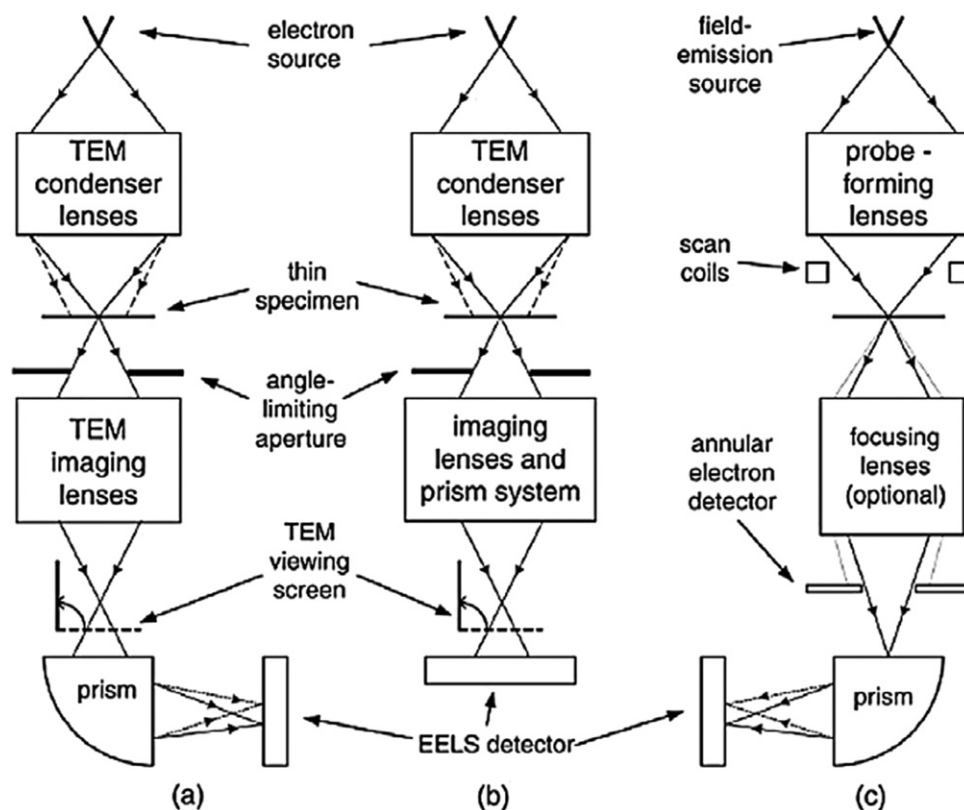


Fig. 1 Standard procedures for EELS acquisition in TEM (a) TEM with a magnetic-prism spectrometer below the viewing screen, (b) TEM incorporating an in-column imaging filter and (c) scanning-transmission (STEM) system. Reproduced from Egerton, R.F., 2009. Electron energy-loss spectroscopy in the TEM. *Rep. Progr. Phys.* 72, 016502. Available at: <https://doi.org/10.1088/0034-4885/72/1/016502>.

The image is formed on a charge-coupled device (CCD) camera. A slit can be introduced to act as an energy-filter. The arrangement of the equipment is shown in Fig. 1(b). A third kind of system is based on STEM. A field emission source is used to form a probe that can raster scan the specimen. A dark field image is generated by highly scattered electrons that are collected at a ring-shaped (annular) detector. The annular detector read-out should be synchronous to the scanning probe.

Background: EELS Spectrum

Analysis of the core-loss ionization edges allows the user to determine the chemical composition from EELS. The spectrum is due to both multiple elastic and inelastic scattering of the electrons by the sample. EELS spectra are complex in nature due to the presence of the zero-loss peak (ZLP), energy-loss near edge structure (ELNES), extended electron energy-loss fine structure (EXELFS) (Ahn, 2005), plasmon inter-band transitions (Raether, 1980) and phonon scattering etc. These influence the extraction of core-loss edges through background subtraction. In the low-loss region (Browning *et al.*, 2011) of an EELS the predominant feature is the ZLP due to the combination of both elastic scattering and phonon scattering. The energy-loss of phonon scattering is so low that it is almost impossible to resolve in conventional spectrometers (Baden *et al.*, 1981) and only very recently highly stabilized spectrometers with energy resolution < 30 meV have become available (Krivanek *et al.*, 2013). In recent years, phonon extraction from ZLP has been proposed (Egoavil *et al.*, 2014) by either subtracting or dividing the modeled ZLP from the experimental spectra. The ZLP is mostly forward scattered and very intense so sometimes it tends to saturate the CCD due to its high intensity. The other prominent feature in the low-loss range is the plasmon loss as shown in Fig. 2.

This is due to polarization of the material by the passing high-energy electrons. The typical range of energy-loss of bulk plasmon peaks is from 1 eV to ~ 30 eV (Williams and Carter, 1996). Multiple bulk plasmon losses can occur if the sample is thicker. Also surface plasmons in very thin films can occur (Scholl *et al.*, 2012). Since the surface plasmon effects are only due to polarization on surface, it is a 2D effect unlike bulk plasmon which is due to bulk material (3D). This also mean the location of surface plasmon can be approximated if bulk plasmon is known. i.e., $E_p \approx E_s \times \sqrt{2}$. The peak of a plasmon shifts with respect to the dielectric properties of the material and the complex dielectric constant can be extracted from the single scattering distribution via Kramers-Kronig transform. The study of shifts in bulk plasmon peaks is important in characterizing the alloys (Williams and Carter, 1996). The change in peak position with respect to composition, x , can be modeled as shown in Eq. (1), where x denotes

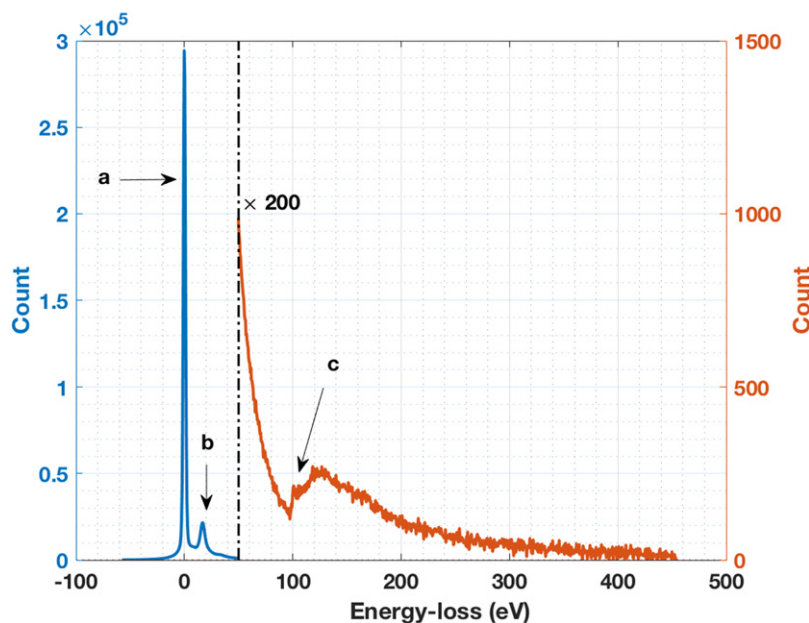


Fig. 2 A low-loss electron energy-loss spectrum of polycrystalline Si. (a) ZLP (b) bulk plasmon peak (c) Si $L_{2,3}$ ionization core-loss edge on top of exponential decaying background. Experimental conditions: voltage = 197 kV, dispersion = 0.5 eV per channel, spectrum offset = 0 eV, exposure time = 0.1 s.

the composition ratio in a binary alloy.

$$E_p(x) = E_p(x=0) + x \cdot \left(\frac{dE_p}{dx} \right) \quad (1)$$

The peak position of the bulk plasmon can be interpolated by least squares fittings as was proposed by Hunt *et al.* (1995). The ELNES provides the bonding information which can be used to calculate chemical shifts (Kimoto *et al.*, 1997; Mayer and Plitzko, 1996; Reimer, 1995; Wang *et al.*, 2018) and maps of these shifts can be obtained (Thomas and Midgley, 2001a; Thomas *et al.*, 1999; Walther *et al.*, 1995), whereas the EXELFS provides the diffraction effects surrounding the ionized atom due to excess energy of the ionized electron. In the high-loss region EEL spectra have a background that is decaying almost exponentially. The core-loss edges superimposed on this background can be extracted and the influence of multiple plasmon scattering can be removed by Fourier-based deconvolution (Thomas and Midgley, 1999, 2001b) with the low-loss function, yielding single scattering distribution. The extracted core-losses can be mapped to obtain relative concentration maps (Cooper *et al.*, 2011; Muller *et al.*, 2008) or absolute atomic density distribution maps (Colliex *et al.*, 2010, 1994; Pennycook *et al.*, 2011).

Ionization Edges

The automated ionization edge detection can be modeled by either identifying local positive gradients or by peak detection of positive gradients. The quantification of EELS used in here follows the standard integration method (Egerton, 1978). To quantify a spectrum there are a lot of challenges in terms of artifacts, noise and gain correction problems of the CCD camera. Hence, a pre-treatment of spectra is necessary before the process of edge detection and background subtraction. If the background is exponentially decaying, there is no ionization edge and the SNR is high, then the gradient of a spectrum should be negative everywhere. As the spectrum is preprocessed, positive gradients indicate the presence of core-loss edges. A look-up table can be used to accurately identify the corresponding core-losses of the elements. An inverse power-law or exponential decay function will be used to fit a curve, $B(E)$, in the pre-edge region to fit, extrapolate and subtract the background. The extracted core-loss edges are used for further quantification using integration after background subtraction. A spectrum $S(E)$ with ionization edges superimposed on a background modeled by $B(E)$ at higher losses as a function of energy-loss (E) and integration range (Δ) is shown in Eq. (2). I is the intensity and σ the ionization cross-section for the j^{th} shell of i^{th} element in the spectrum.

$$S(E, \beta, \Delta) = B(E) + \sum_{ij} I_{ij}(\beta, \Delta) \sigma_{ij}(\beta, \Delta) \quad (2)$$

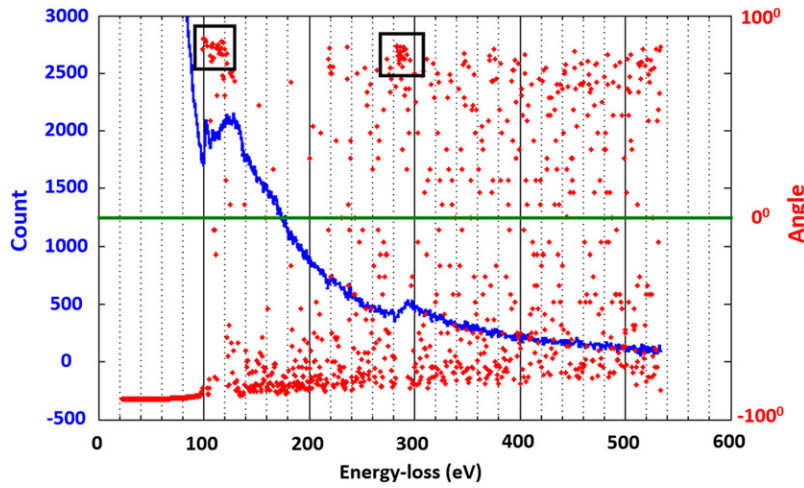


Fig. 3 Original spectrum of Si $L_{2,3}$ edge and C K edge (in dark blue) and angle as defined in Eq. (8) (in red) showing the presence of clusters in the latter correlates with the onset of ionization edges.

Detection of Ionization Core-Loss Edges

For automation of background subtraction, a novel approach of core-loss edge detection is proposed. For an EELS spectrum image (SI), $S(x, y, E)$, the gradient of SI can be defined as shown in Eq. (3).

$$\nabla S = \left[\frac{\partial}{\partial x} \hat{x} + \frac{\partial}{\partial y} \hat{y} + \frac{\partial}{\partial E} \hat{E} \right] S(x, y, E) \quad (3)$$

where ∇S is the gradient of the SI (data cube) with regard to spatial $\hat{x}$, $\hat{y}$ directions and energy-loss direction $\hat{E}$. The gradient of the EELS SI, $S(x, y, E)$, in the direction of energy loss is determined by Eq. (4).

$$\nabla S \cdot \hat{E} = \frac{\partial}{\partial E} S(x, y, E) \quad (4)$$

Numerically, a gradient is the central difference for the inner channels in the $\hat{E}$ direction as shown in Eq. (5).

$$(\nabla S)_{E_n} \cdot \hat{E} = \frac{1}{2} \cdot \{S(x, y, E_{n+1}) - S(x, y, E_{n-1})\} \quad (5)$$

where $n \in \mathbb{N}_1$: $1 < n < N$ and $N \in \mathbb{N}$ is the number of channels (or length of the spectrum). The gradient of the spectrum at the end of channels are single sided differences as shown in Eq. (6) for $n = 1$ and Eq. (7) for $n = N$.

$$(\nabla S)_{E_1} \cdot \hat{E} = S(x, y, E_2) - S(x, y, E_1) \quad (6)$$

$$(\nabla S)_{E_N} \cdot \hat{E} = S(x, y, E_N) - S(x, y, E_{N-1}) \quad (7)$$

The gradient of EELS has to be negative for ranges beyond multiple plasmon losses and without any core-losses, will be falling asymptotically towards zero. The only points that show positive gradient must be due to the presence of noise or ionization edges. If the EELS SI is denoised, the probability of a positive gradient being due to shot noise is low, although clearly dependent on the type of denoising method used. The angle (θ) between the EELS and horizontal energy axis is determined by Eq. (8) and can be plotted, as shown for an example spectrum of Si with C in Fig. 3.

$$\theta = \arctan\{\nabla S \cdot \hat{E}\}, -\frac{\pi}{2} < \theta < \frac{\pi}{2} \quad (8)$$

The arctan (a.k.a $\tan^{-1}\{\cdot\}$) function can bifurcate the gradients by flushing them far apart to $-\pi/2$ for background gradient and $\pi/2$ for gradient at edge onset making the onset detection more reliable. Only positive angles are considered further, as negative values are due to the background of EELS. A cluster of positive angles is formed if a core-loss edge is present. Positive angle values without a cluster are due to noise. A similar gradient approach of ionization edge detection by applying derivatives to log of spectrum was proposed by Kundmann and Krivanek (1991) and was extended to EELS SI by Thomas (2001). The algorithm had problems with severe noise levels in ELNES and EXELFS. This makes the onset detection difficult if the ionization core-loss edges are in close proximity.

Cluster Detection by Counting Positive Slope Angles

Clusters are detected by counting the positive angular data points within a window, compared to the size of the window. The flow chart for the process implemented in Matlab is shown in Fig. 4. The mod (or modulo operator) is defined in Eq. (9) (Knuth, 1973).

If the length of the spectrum, $N \in \mathbb{N}$, is not a multiple of the size of the window, $w \in \mathbb{N}$, there will be a few pixels left at the end of last iteration. These reminder pixels, $r \in \mathbb{N}$, can be taken as window size at the end of the spectrum, or they can be ignored. But if the dispersion has been binned to a large value or the chosen window size is larger, then the reminder pixels should not be ignored.

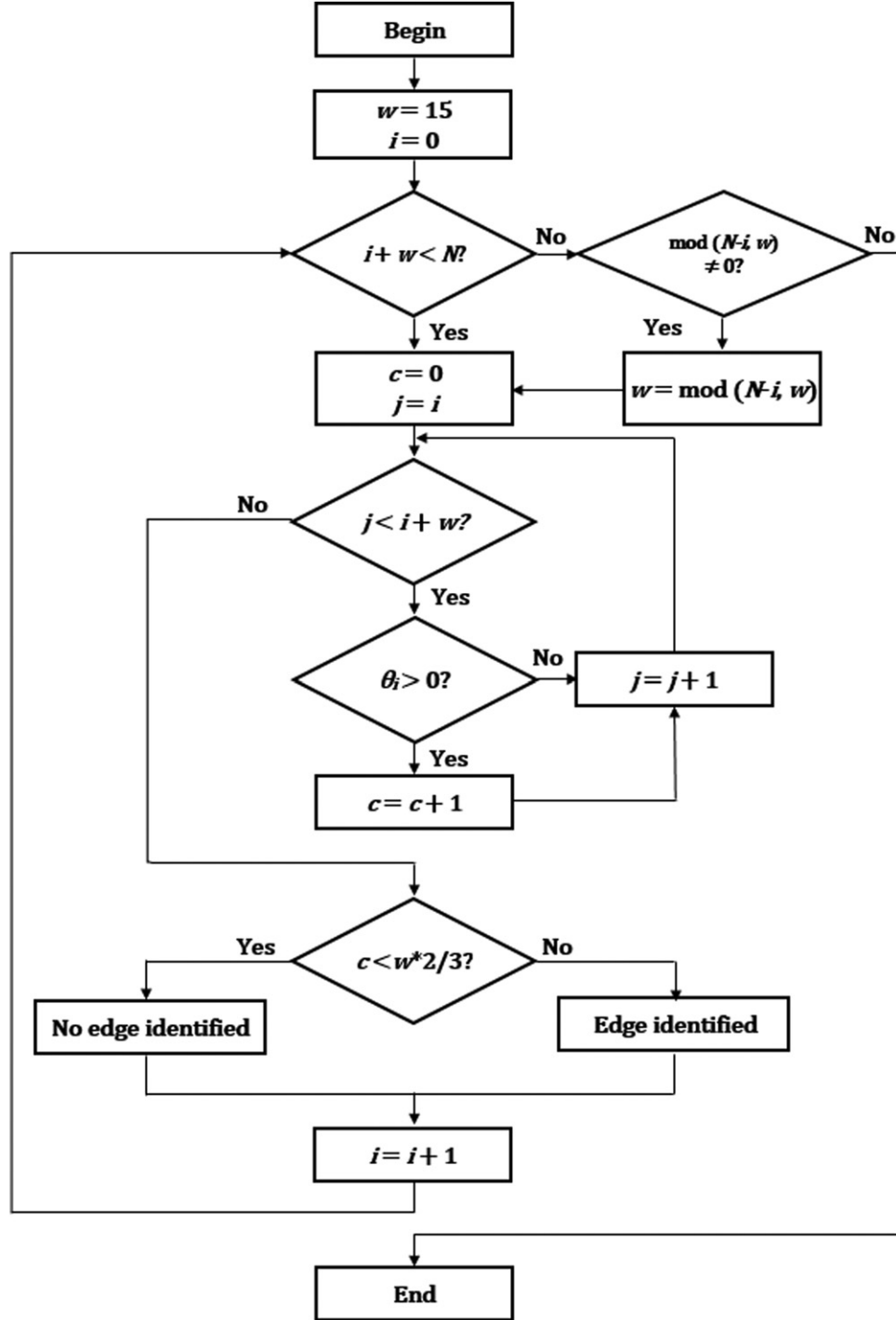


Fig. 4 Flow chart for edge detection in spectra that consist of N channels. c is the count of channels with positive gradient, i is the energy channel, j is the loop count, w is the window width and mod is modulo operator (remainder after division).

$$r = N - w \cdot \left\lfloor \frac{N}{w} \right\rfloor \quad (9)$$

Table 1 A look-up table used for edge detection. (*h* = hydrogenic edge, *d* = delayed onset and *w* = white lines)

<i>Z</i>	<i>Edges</i>	<i>Onset in eV</i>	<i>Edge shape</i>	<i>Edge type</i>
5	B K	188	<i>h</i>	K
6	C K	284	<i>h</i>	K
7	N K	400	<i>h</i>	K
8	O K	532	<i>h</i>	K
9	F K	685	<i>h</i>	K
13	Al K	1560	<i>h</i>	K
13	Al L ₁	118	<i>h</i>	L
13	Al L ₃	73	<i>d</i>	L
14	Si L ₃	100	<i>h</i>	L
15	P L ₁	189	<i>h</i>	L
15	P L ₃	135	<i>d</i>	L
16	S L ₁	229	<i>h</i>	L
16	S L ₃	165	<i>h</i>	L
17	Cl L ₁	270	<i>h</i>	L
17	Cl L ₃	200	<i>d</i>	L
19	K L ₁	377	<i>h</i>	L
19	K L ₃	294	<i>w</i>	L
29	Cu L ₃	931	<i>h</i>	L
30	Zn L ₃	1020	<i>d</i>	L
31	Ga L ₃	1115	<i>d</i>	L
32	Ge L ₃	1217	<i>d</i>	L
33	As L ₃	1323	<i>d</i>	L
47	Ag M ₅	367	<i>d</i>	M
49	In M ₅	443	<i>d</i>	M
65	Tb M ₅	1242	<i>w</i>	M

The floored division operator $\lfloor \cdot \rfloor$ gives the integer part of $\frac{N}{w} \in \mathbb{R}$. The size of the window is chosen such that it should be comparable to the sharpness of the onset of typical edges (a few eV for sharp hydrogenic and up to 10 eV for delayed edges). Similarly, the window size should not be too small (< 5 channels), to avoid false positives due to noise. Typically, the window sizes selected in this study were between 5 and 25 channels wide (the default is $w = 15$), and clusters are identified as intervals of that given width wherein at least 2/3 of all channels have angular values $\theta > 0$. Due to near edge structures or/and chemical shifts the edges detected may not be at the exact location of the ionization onset predicted for free atoms. It may also happen that 2 or 3 consecutive windows might detect positive angles. To refine the results from ionization edge identification, a look-up table is used containing onset values of some of the major ionization edges (Ahn *et al.*, 1983; Egerton, 2011) as shown for some elements relevant for semiconductors in Table 1¹. The exact edge onset is identified from the predicted edge positions (clusters) by finding the nearest ionization edge in the look-up table that agrees with position of the beginning of the window, as shown in Eq. (10):

$$Edge_i = E_{(\min||E_n - Cluster_i||)} \quad (10)$$

where E_n is the list of all n ionization edges from the look up table, $Cluster_i$ is the list of all predicted ionization edge onsets (numbered consecutively by index). The ionization edge detection and correction can be visualized as shown in Fig. 5. Histograms of the detected edges in three different EELS SI of a cross-sectioned multi-junction solar cell are shown in Fig. 6. Although edge onset identification may fail in individual spectra due to noise the histograms clearly show that the identification of the edges is unambiguous when thousands of spectra from all locations in SI are considered. The efficiency of the edge detection is also dependent on the quality of the gain correction of the CCD. Long exposures of the ZLP might yield artifacts in successively acquired spectra due to gain changes induced by over exposures. This could potentially lead to false positive detection of ionization edges in EELS acquired with energy offsets. Such artifacts can, however, be identified by varying the energy offset as they remain fixed at that channel (usually around #100) where the ZLP had been placed before. A multi-junction solar cell is used for the detection and quantification of all the ionization core-losses using cluster detection by identifying the positive cluster of gradients.

Cluster Detection Through Peak Detection

Another method of detecting the clusters is by predicting the kind of statistics these clusters exhibit. The clusters are formed due to the presence of edge onsets and tend to have positive slope angles. All the negative values are due to the presence of strong background. This indicates that the mean value of a group of clusters is always higher than the rest of the pixels and can be detected by an

¹Note: The table only lists some of the major semiconductor ionization onsets. Due to anomalies in the CCD gain correction, some of the ionization onsets were wrongly detected. Hence few of the uncommon elements and semiconductor material were not considered.

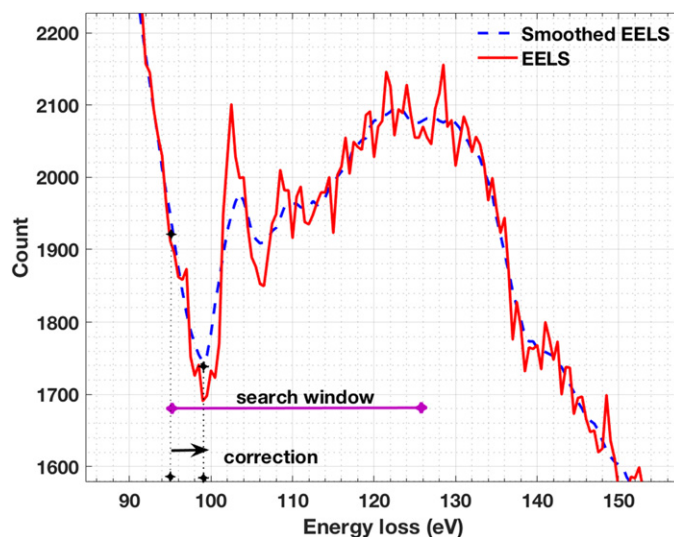


Fig. 5 The location of core-loss (here: Si $L_{2,3}$ edge) is detected from the look-up table and fine-tuned to a value of 99 eV as per Eq. (10).

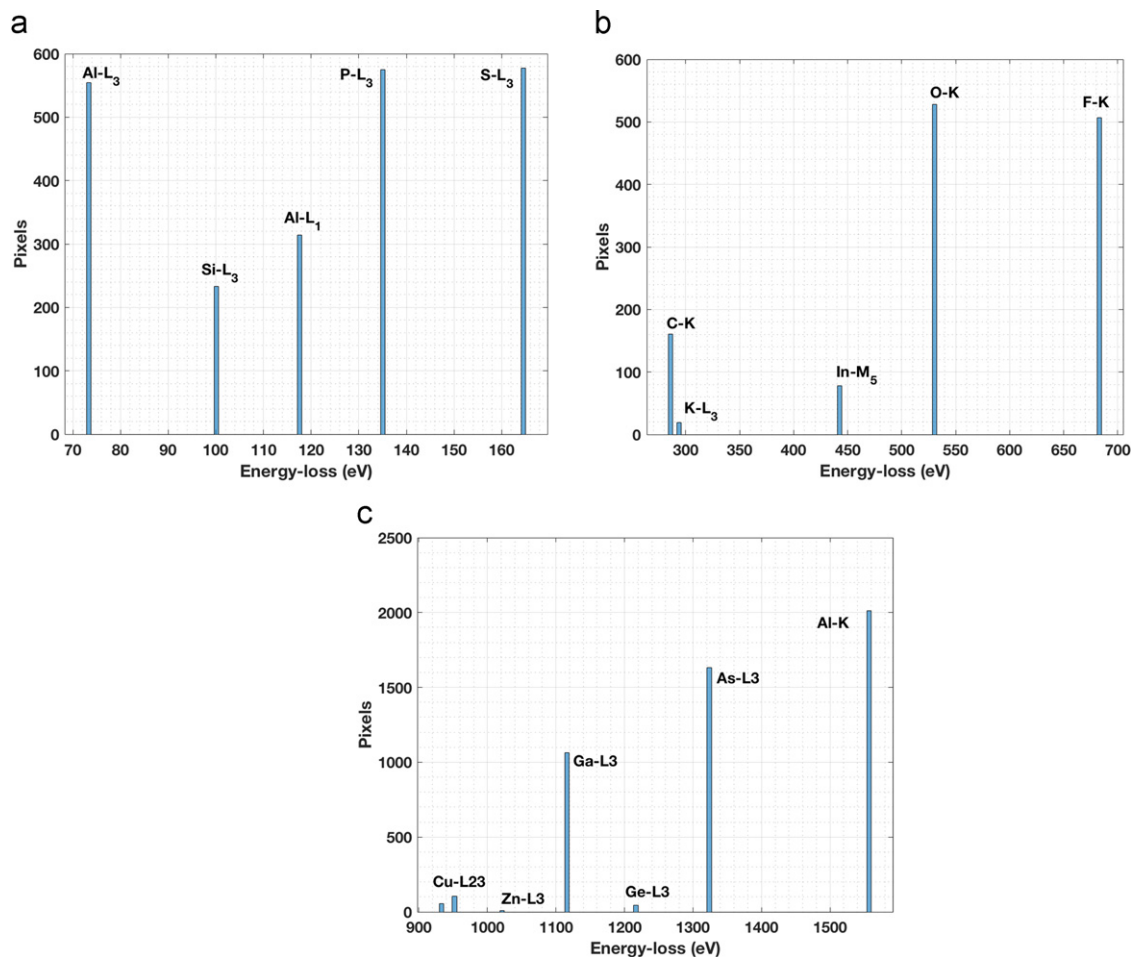


Fig. 6 Histogram distribution of edge onsets detected for EELS Si from semiconductor heterostructure shown in Angadi, V.C., Abhayaratne, C., Walther, T., 2016. Automated background subtraction technique for electron energy-loss spectroscopy and application to semiconductor heterostructures. *J. Microsc.* 262, 157–166. Available at: <https://doi.org/10.1111/jmi.12397>, Fig. 7 for 80 eV offset (a), 250 eV offset (b) and 950 eV offset (c).

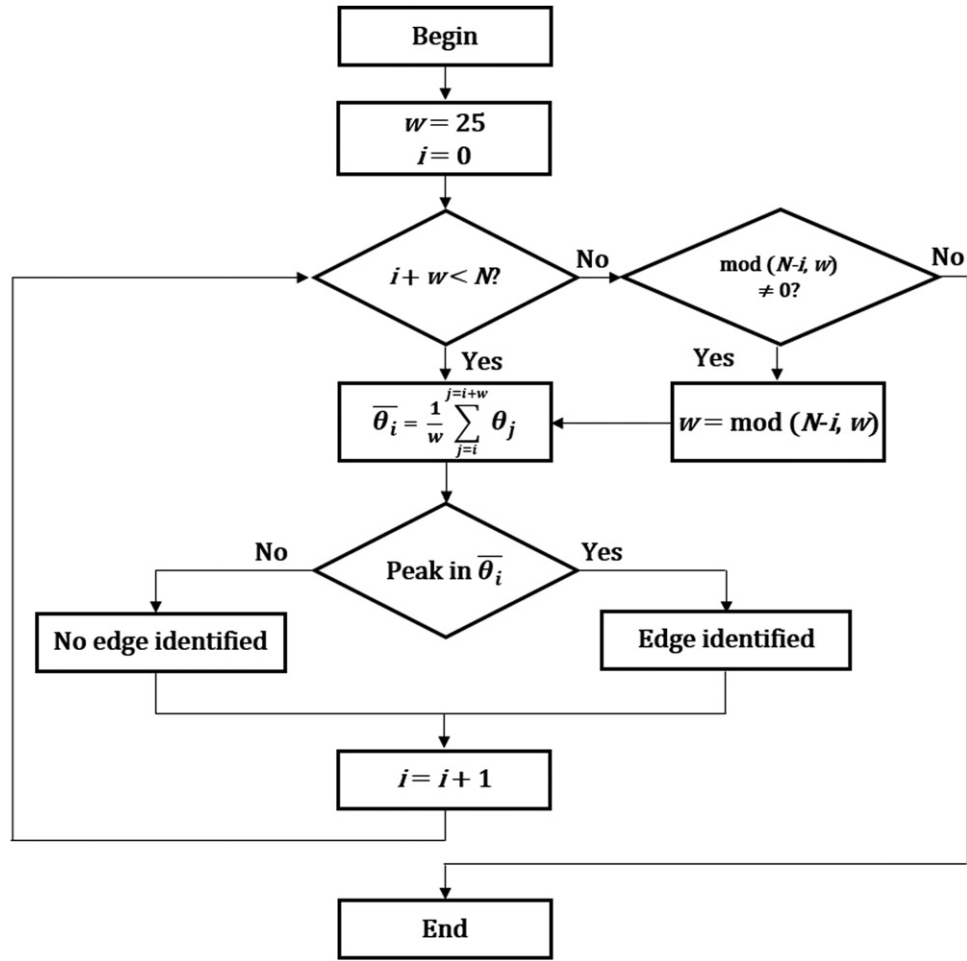


Fig. 7 Flow chart for edge detection in spectra that consist of N channels. $\bar{\theta}_i$ is the mean value of angles, i is the energy channel, j is the loop count, w is the window width and mod is modulo operator (remainder after division).

$$\hat{r}(E) \approx \frac{\nabla S \cdot \hat{E}}{B(E)} \quad (11)$$

$$\theta = \arctan\{\hat{r}\}, -\frac{\pi}{2} < \theta < \frac{\pi}{2} \quad (12)$$

overlapping sliding window of size $w \in \mathbb{N}$. The implementation of this algorithm is shown in Fig. 7 as a flowchart. Unlike θ from Eq. (8), slope angles are calculated by estimating the exponent r from inverse power-law function (or the exponent from exponential decay function) at each channel if the pre-edge region is already known (Eq. (12)). The value of r is estimated as shown in Eq. (11).

$\bar{\theta}$ can be viewed as the θ value smoothed over a window of w . It is important to apply a Hampel filter to remove single pixel noise which may be misinterpreted as an ionization edge prior to the above evaluation. Applying a Hampel filter ensures that θ values only contain features from core-loss edges. Consider the example of a spectrum as described in Eq. (2), with two ionization edges $\sigma_1(E, \beta)$ and $\sigma_2(E, \beta)$ and an inverse power-law function as a model for the background as described in Eq. (13).

$$S(E, \beta) = A \cdot E^{-r} + I_1 \cdot \sigma_1(E, \beta) + I_2 \cdot \sigma_2(E, \beta) \quad (13)$$

The term $-E^{-1}$ in Eq. (14) provides the baseline for $\hat{r}(E)$ and it is almost constant at high enough energy-losses. The term after the addition sign in Eq. (14) provides the features describing the edge onset as shown in Figs. 8 and 9. The r term is the exponent of the background of the spectrum, $S(E, \beta)$.

$$\hat{r}(E) \approx r \cdot -E^{-1} + A^{-1} \cdot E^r \left[I_1 \frac{\partial}{\partial E} \sigma_1(E, \beta) + I_2 \frac{\partial}{\partial E} \sigma_2(E, \beta) \right] \quad (14)$$

If there is no knowledge of pre-edge regions, then θ can be calculated as previously described in Eq. (8). The window size is typically chosen from $w = 5$ to 35. At each sliding window a mean value of slope angles $\bar{\theta}$ is calculated at each energy channel i .

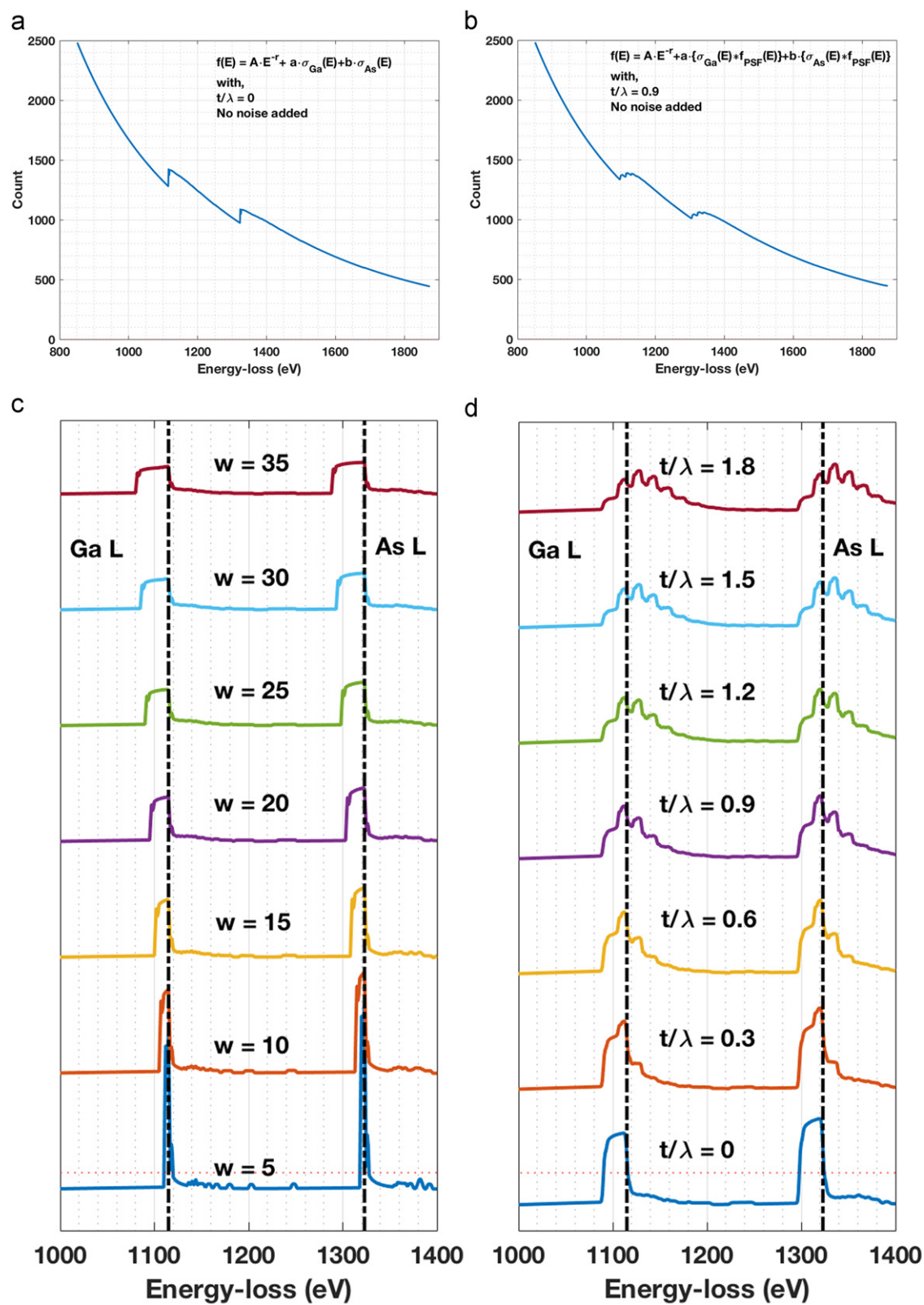


Fig. 8 Simulated GaAs spectra using two Hartree-Slater cross-sections for Ga L and As L respectively with (a) $t/\lambda = 0$ (b) $t/\lambda = 0.9$, $w = 25, A = 3.75 \times 10^{10}, r = 2.45, a = b = 25$. Dependence of Ga L and As L edge detection (c) with variable size of the window, w for $t/\lambda = 0$. (d) as a function of relative thickness.

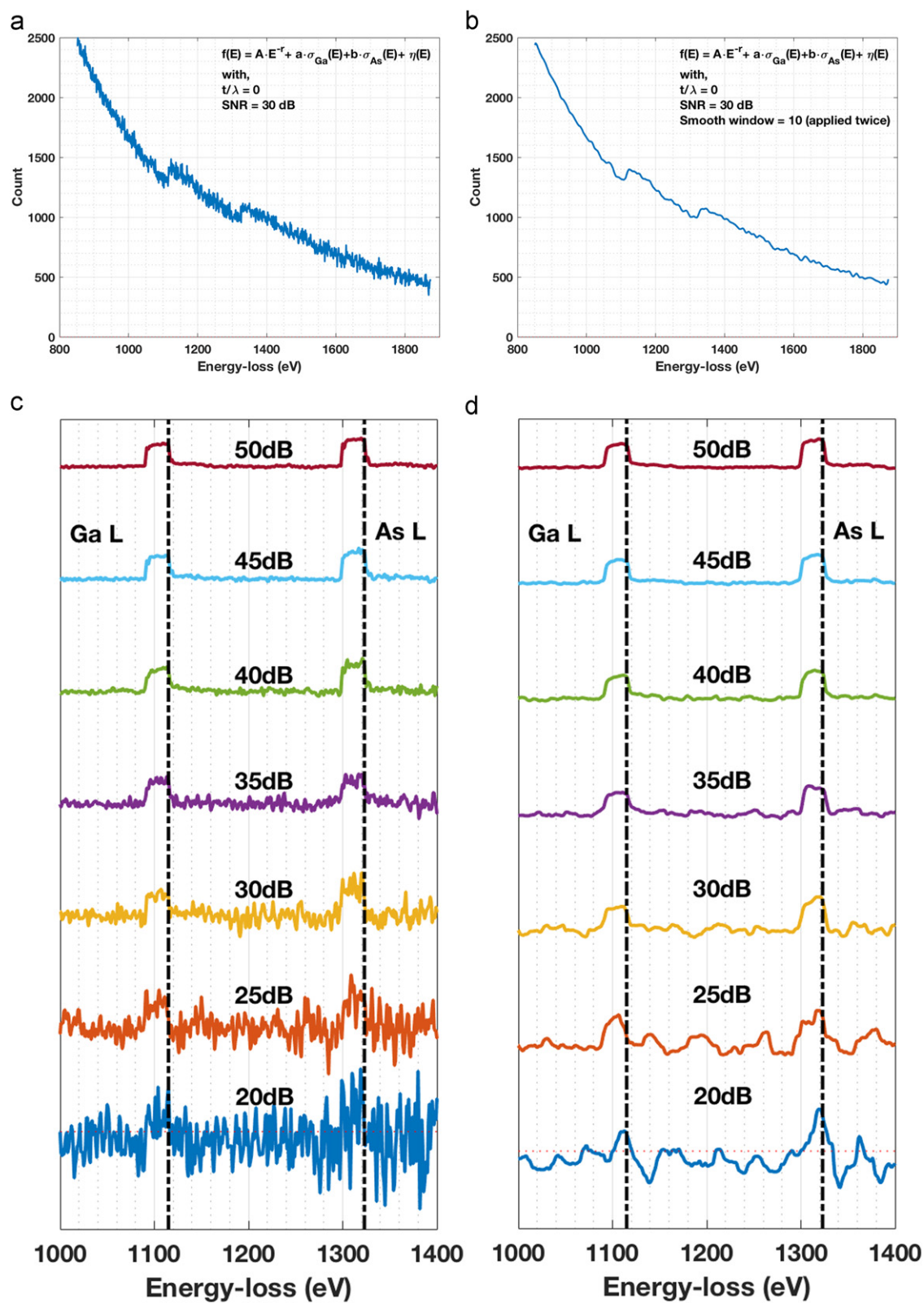


Fig. 9 Simulated GaAs spectra using two Hartree-Slater cross-sections for Ga L and As L respectively with (a) 30 dB, (b) 30 dB and smoothed using twice an averaging filter of window size 10. $t/\lambda = 0$, $w = 25$, $A = 3.75 \times 10^{10}$, $r = 2.45$, $a = b = 25$. Dependence of Ga L and As L edge detection (c) with addition of white Gaussian (AWG) noise at varying SNR for $w = 25$ and $t/\lambda = 0$ and (d) the smoothed AWG noisy spectrum filtered with an averaging filter of width 10 pixels at varying SNR.

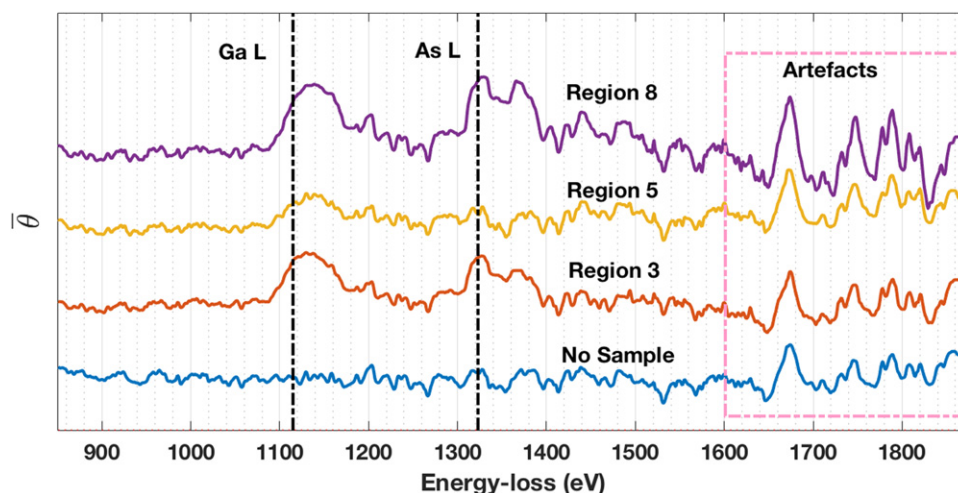


Fig. 10 The edge detection by cluster method ($w = 25$) applied to sum spectra from regions 8, 5, 3 and a region without sample of multi-junction solar cell described in Angadi, V.C., Abhayaratne, C., Walther, T., 2016. Automated background subtraction technique for electron energy-loss spectroscopy and application to semiconductor heterostructures. *J. Microsc.* 262, 157–166. Available at: <https://doi.org/10.1111/jmi.12397>, Fig. 7(b). Each $\bar{\theta}$ spectrum has a vertical range between $-\pi/2$ to $\pi/2$.

The window sliding is done one channel at a time. A similar technique of including residue channels in subsection “Cluster Detection by Counting Positive Slope Angles” is incorporated using the mod operator. The position of falling edge of the peak in $\bar{\theta}_i$ is the nearest estimate of the onset of the core-loss ionization edge. The robustness of the technique can be studied by simulating a GaAs high-loss spectrum and applying the method described in Fig. 7 with varying size of the sliding window (w), relative thickness (t/λ) and the noise level. A spectrum, $S(E, \beta)$, is simulated by an inverse power-law function (AE^{-r}) and the theoretical cross-sections of Ga $L_{2,3}$ and As $L_{2,3}$. To test the effect of varying window size, w , a spectrum has been simulated with $t/\lambda = 0$ without noise. Fig. 8(c) shows that the position of the peak which indicates the ionization core-loss remains at the same position as the size of the window, w , is increased from 5 to 35 channels. However, the peak is broadened towards lower energy-loss with increase in w . This is because the window slides from left to right of the energy-loss axis. A similar effect of peak spreading towards higher energy-loss is observed when sliding the window instead from right to left of the energy-loss axis. However, the falling edge of the peaks remain approximately at the edge onset (Ga L at 1115 eV and As L at 1323 eV) and the rising edges remain in place for windows sliding from right to left. In Fig. 8(c), it appears as if, using a smaller w is better because the peak remains unambiguously located at the edge onset. However, due to noise present in the experimental spectrum, using smaller w will have a noises $\bar{\theta}_i$ and the detection of peak becomes more unreliable. If the SNR of the spectrum is high, it is possible to detect L_2 and L_3 edges, as seen in Fig. 8(c) for $w = 5$. To test the effect of varying relative thickness, t/λ , the simulated GaAs single scattering spectrum (with no noise added) is convoluted with a low-loss, $f_p SF(E)$, to simulate a spectrum from thicker GaAs. The relative thickness, t/λ , is varied from 0 to 1.8, in steps of 0.3. The low-loss is simulated by a Gaussian for ZLP and Lorentzian functions for bulk plasmon peaks weighed according to Poissonian statistics. Fig. 8(d) shows that for $t/\lambda = 0$, the peak detected at ionization onset has same energy spread as the FWHM of ZLP. As t/λ is increased to 1.8, the multiple peaks that appear in Fig. 8(d) are peaks due to multiple scattering. Hence for a thicker specimen, mere detection of maximum peak location is not a precise detection of edge onset. These peaks due to multiple scattering are spaced at multiples of the bulk plasmon energy ($E_p = 15.7$ eV). Hence, for a thicker sample the ionization edge detection might be off by multiples of E_p . The single scattering spectrum can be obtained by deconvolution. The edge correction as discussed previously for high-loss ionization edges. This is because at high-loss the ionization edges are far apart and the relative accuracy and efficiency of a precise edge detection will be higher. The SNR of the EELS spectrum decreases with increase in energy-loss. This will have a large effect on detecting edges as the heights of the ionization edges become comparable with the amplitude of noise. An additive white Gaussian noise (AWGN), $\eta(E)$, is added to the simulated spectrum to test the effect of noise level on the detection of Ga $L_{2,3}$ and As $L_{2,3}$. The SNR is calculated using Eq. (15).

$$\text{SNR} = 10 \cdot \log_{10} \left(\left| \frac{\sum_{i=1}^n S_i(E)^2}{\sum_{i=1}^n (S_i(E) - \eta_i(E))^2} \right| \right) \quad (15)$$

From Fig. 9(c), it is evident that peak detection gets difficult for spectra with SNR < 30 dB. Once the simple averaging filter is applied the peak detection can be made reliable up to ~ 25 dB, as shown in Fig. 9(d). To make sure the spectrum has high enough SNR for detecting core-loss edges, one way is to get the sum spectrum (or mean spectrum) from regions in an EELS SI and calculate the $\bar{\theta}$ as in Eq. 8. Getting sum spectrum can be automated if the overview image has distinct contrasts. Then the sum spectra can be obtained from regions identified by image segmentation algorithms. This improves the counting statistics for the spectrum and reduces Poissonian noise significantly. The edge detection by cluster method by means of finding peak position has been applied to different semiconductors described in Angadi et al. (2016), Walther et al. (2017) and Angadi et al. (2017). The sum spectra from

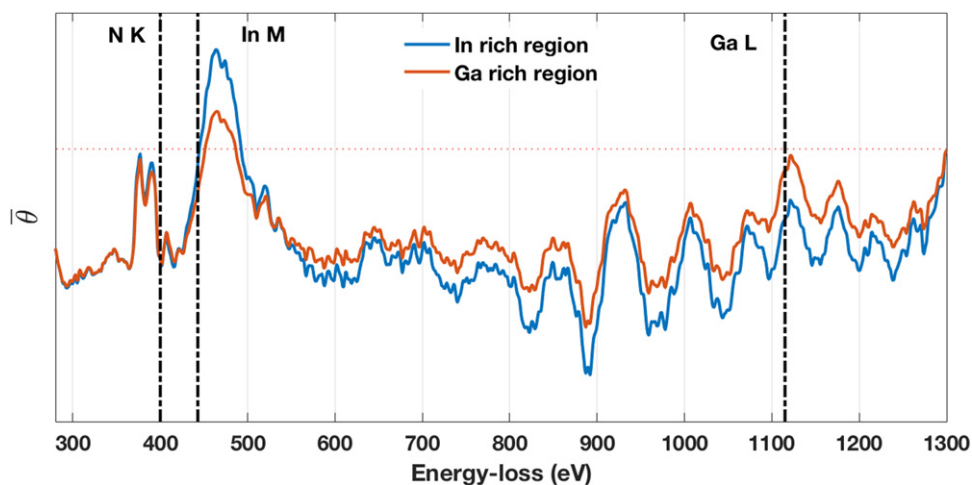


Fig. 11 The edge detection algorithm ($w = 25$) is applied to In x Ga 1-x N phase separated material. Sum spectrum is extracted from In rich and Ga rich region from EELS SI. Each $\bar{\theta}$ spectra have vertical range between $-\pi/2$ to $\pi/2$.

regions 8, 5, 3 and a region with no material (all spectra above region 1) from multi-junction solar cell with SI of 950 eV spectrum offset are considered in order to check if all the edges are identified. The edges that are expected from 950 eV offset SI are Ga $L_{2,3}$ edge at 1115 eV, As $L_{2,3}$ edge at 1323 eV and Al K edge at 1560 eV. As expected both Ga $L_{2,3}$ and As $L_{2,3}$ are identified from GaAs regions (regions 3 and 8). Region 5 is expected to be AlGaInP, hence no As $L_{2,3}$ is identified. All the $\bar{\theta}$ spectra from Fig. 10 show the features of ionization edge except for the $\bar{\theta}$ spectrum with no material. It is interesting to note the features shown in the pink box in Fig. 10 are artifacts present in all regions of the SI. These are specific to particular channels of the spectrum and probably due to anomalies in the gain correction. Minute changes in the $\bar{\theta}$ can be observed across all the spectra in Fig. 10 for all regions. But large peaks are observed at channel numbers 824, 898 and 939. These artifacts will also mask a possible Al K edge at 1560 eV. Hence, Al K edge cannot be detected. The edge detection algorithm from Fig. 7 is tested with In_x Ga_{1-x} N material with sum spectrum extracted separately from In and Ga rich regions² to check the extent of variation in edge detection with varying concentration of In and Ga. The $\bar{\theta}$ spectra for both In and Ga rich are superimposed in Fig. 11. Similar to previous findings, the $\bar{\theta}$ is affected by anomalies in the gain correction. It is noticeable in both spectra. In In_x Ga_{1-x} N material, the percentage of N would be constant but the percentages of In and Ga can change. This is also reflected in $\bar{\theta}$ spectra as N K edges overlap almost perfectly in both spectra from In and Ga rich In_x Ga_{1-x} N. The Ga $L_{2,3}$ edge in the In rich spectrum is difficult to identify due to effects from gain correction and the intensity of the edge onset is very low. However, in Ga the rich region, the Ga $L_{2,3}$ edge is clearly identifiable and the In $M_{4,5}$ intensity is lower. Hence the stoichiometry also plays an important role in identifying the ionization edges from clusters. It is also worth noting that if the ionization edge onset is hydrogenic (as in case of N K edge) or sharp as in single scattering (as shown in Fig. 8(c)) then the edge onset is the falling edge of peaks in $\bar{\theta}$ spectrum which was observed in Fig. 8(c). However, if the edges are delayed (as in In $M_{4,5}$) and/or plural scattered then the true edge onset is near the rising edge as observed in Fig. 8(d). The thicker the sample, the more intensity is redistributed to higher energies hence the onset must be changed to rising edge instead of falling edge. The algorithm has finally been applied to Tb doped AlN material (Angadi *et al.*, 2017). Two sum spectra are extracted³ from Box A (AlN) and Box B (Si substrate) as shown in Angadi *et al.* (2017), Fig. 3(f). The span of the energy-loss is from 340.8 eV to 1614.8 eV. Hence, the large energy-loss span is responsible for the visible background following a $-E^{-1}$ trend from Eq. (14). The N K and O K are sharp hydrogenic edges, hence the edge onset is at the falling edge of the peaks. Tb $M_{4,5}$ edge at 1242 eV is present but it is not detectable due to the fact that its concentration in AlN is ~ 2 at% (Benz *et al.*, 2013) and the height of edge onset is comparable with noise at high-loss. Also, during acquisition, the spectra were binned by a factor 4 to reduce the size of data set in energy-loss direction from 2048 to 512 channels making the dispersion to 2.8 eV/channel rather than 0.7 eV/channel. The white lines from $M_{4,5}$ transition of Tb₂O₃ complex are at 1243 eV for M_5 and 1274 eV for M_4 about 30 eV apart with FWHM of ~ 4 eV. The energy dispersion of the spectrum is 2.8 eV/channel. Benz *et al.* (2013) have shown high-loss EELS spectra with 800 eV spectrum offset, 1 eV/channel dispersion and 100 exposure time for 2% Tb doped in AlN. The ionization edge height is still very low, even for 100 s. Hence, for 2.8 eV/channel dispersion with 0.1 s exposure time, there are only 1 or 2 pixels that might describe the white lines. Also as discussed earlier, the stoichiometry also plays major role in identifying the edge onset. The algorithm detects clusters not a single pixel. Hence, the single pixels are treated as an outlier, i.e. noise. Apart from white lines, the ionization edge property of Tb $M_{4,5}$ is wide and delayed. Hence, Tb $M_{4,5}$ is not detectable in this particular SI. The sum spectrum from AlN region has been obtained by averaging ~ 3741 spectra, whereas sum spectrum from Si substrate is obtained by averaging ~ 1131 spectra. This means that the SNR of the AlN sum spectrum should be higher than the one from the Si sum spectrum. The noisy

²The In and Ga rich regions can be seen in elemental maps shown in Fig. 2(e, g) Walther, 2016.

³In the high-loss SI of AlN doped with Tb, first #10 and last #50 channels have been distorted (cut-off) to zero value while acquisition. This could be due to the energy slit introduced. Hence all the spectra are considered from channel numbers #11 to #467 only.

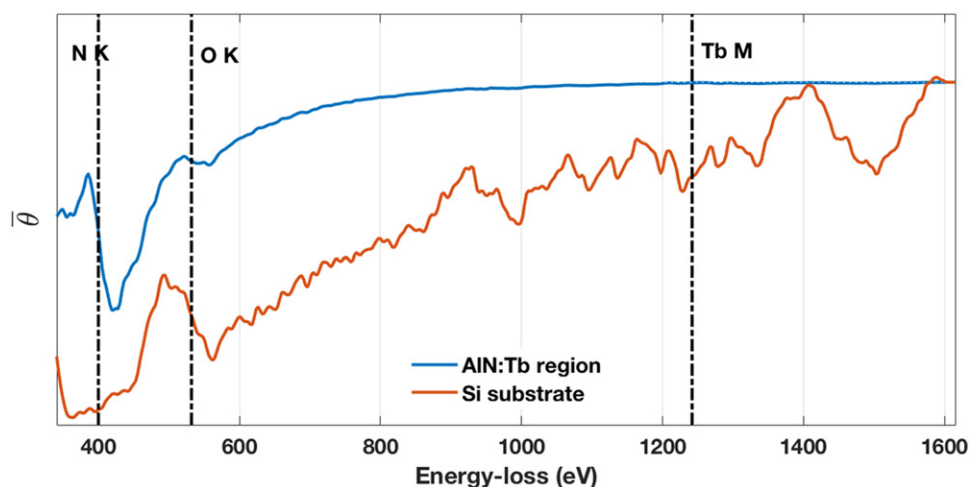


Fig. 12 The edge detection algorithm is applied to Tb doped AlN EELS SI. The sum spectrum (~ 3741 spectra) are taken from AlN Box A as in Angadi *et al.*, Fig. 3(f) and another sum spectrum (~ 1131 spectra) from Si substrate region which is indicated as Box B in Angadi, V.C., Benz, F., Tischer, I., et al., 2017. Evidence of terbium and oxygen co-segregation in annealed AlN:Tb. Appl. Phys. Lett. 110, 222102. Available at: <https://doi.org/10.1063/1.4984237>, Fig. 3(f).

artifacts present for the latter in Fig. 12 is evidence of SNR being lower. $\text{In}_x\text{Ga}_{1-x}\text{N}$ and AlN doped with Tb are used to test the cluster detection by finding the peak.

Conclusion

Apart from the traditional and well known methods of dealing with noise, such as averaging, median filtering or PCA, an alternative approach to remove spikes arising due to dead pixels in the CCD detector is proposed. The Hampel filter used performs median absolute deviation to identify outliers locally and only replaces outliers with the local median whereas traditional smoothing filters tend to smooth the ionization edges which would adversely affect the ELNES. If the absolute residue between spectrum and the local median, $|s_i - m_i|$, is greater than three times the standard deviation (σ_i), then the local median, m_i , is substituted in place of an outlier. Two novel ionization edge detection algorithms are proposed to blindly detect core-losses even if the material is unknown. In the first method, the clusters of points with positive gradients near edge onset are detected by counting them. The method also makes use of a look-up table as in Table 1 to make fine adjustment in the edges detected. Cluster detection can detect edges efficiently when the core-loss has a clear, noise-free and positive onset. It was observed in case of Al $L_{2,3}$, that the edge overlapped with an artifact at channel number #100 due to a previously acquired ZLP. In such cases, even though the edge is clearly detected, the quantification maps will be noisy, as in Angadi *et al.* (2016), Fig. 9(a). At lower energies, ionization edge onsets are much closer. Hence, use of smaller counting windows might lead to false positive detection of core-loss edge onsets. The lookup table is modified in this particular case, where Al L_1 is added even though there is no reliable partial cross-section available for quantification. This was done to get an approximate elemental map of Al. The Al K elemental maps were showing large negative values due to the pre-edge region fitting for Al K being severely affected by EXELFS of the preceding As $L_{2,3}$ edge and the Al K intensity was extremely weak. The ionization edge was detected despite noise comparable to the Al K ionization onset but quantification failed. A similar effect was observed for Ge $L_{2,3}$. The Ge $L_{2,3}$ is falsely detected due to a combination of noise and the EXELFS from the preceding Ga $L_{2,3}$ edge. The look-up table method assumes the energy calibration is done correctly before applying edge detection routine. If the energy-loss is not well calibrated then there could be possible false positive detection of edge onsets, especially at lower energies where the edge onsets are close to each other. The P $L_{2,3}$ quantification was affected by limited integration ranges. The edge detection method by counting the positive slope-angle gradient is a novel approach but ineffective when the onset does not have a definitive positive gradient at edge onset. Kundmann and Krivanek (1991)'s approach of log-derivative had similar drawbacks. Hence the second method of edge detection was developed where the arctan function is applied to estimate the exponent for each channel of the spectrum, as in Eq. (12), rather than calculating the gradient itself, as in Eq. (8). This is a more robust way for detecting edge onsets. The results from simulations used simulated or experimental spectra. The efficiency of the edge detection was tested for a variety of parameters, such as window length, noise, specimen thickness and simple averaging filter applied to spectra of various noise level, calculated as shown in Eq. (15). The detected edges were used to quantify the experimental EELS SIs, with a channel width, $w = 25$ pixels. It was observed in Figs. 10, 11 and 12 that the distortion in gain correction has a large impact on determination of edge onset. Both edge detection algorithms work best when the high-loss spectrum has high SNR (> 30 dB), with constant/linear CCD gain correction, high dispersion (to reduce the effect of $-E^{-1}$ background in $\bar{\theta}$) and single scattering distribution (i.e., deconvolved spectra). The automated selection of pre-edge regions and

integration regions avoids any user bias. The selection of pre-edge region is sometimes tricky at lower energies (< 100 eV) as the core-loss onsets are close to each other and the background fitting is affected by EXELFS of underlying core-losses as well as the long tails of the Poissonian distribution of bulk plasmon peaks.

Future Scope

The automated ionization edge detection by counting positive slope angles uses look-up table to detect ionization edge onsets. The look-up table needs to be more comprehensive and should include all semiconductors and their ionization edges. The edge detection by peak detection could be improved so that its sensitivity to gain correction anomalies and EXELFS can be minimized. The background modeling at post-edge region could be extended to multiple overlapping ionization edges to study the statistics of the quantification.

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Terrestrial Availability of UVA Radiance for Photoactivity Excitation Using Solar Radiation

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Abstract

An estimation of the terrestrial availability of ultraviolet (UV) radiation of the solar radiation is important in designing solar panels, many cosmetic and health products, agriculture and environment that utilized UV-active materials. A linear scale for dosage recommended by the World Health Organization (WHO) indicates the risk of potential sunburn. This linear scale, known as the UV index (UVI), is determined from the amount of radiation in the spectral range that includes both sunburn causing and carcinogenic UVB, and sun-tanning UVA. UVI requires to be rationalized for estimating terrestrial availability of UVA for practical applications of UVA active materials such as photocatalysts that can be activated for photovoltaic and photosterilisation conversion of natural light. Based on harmonization of literature data and our own investigation, we elaborate a general guideline of the terrestrial availability of UVA radiation to estimate the minimum and maximum value of UVA radiance that can be used to benchmark the performance of materials active in this region. This general guideline will be highly useful in photocatalyst design and validation under simulated solar UV conditions leading to performance prediction of products when working in natural light.

Nomenclature

CMF Cloud modification factor

DSSC Dye sensitized solar cells

EUUV Extreme ultraviolet lithography

h Hour

J Joule

m Meter

m a.s.l. Meters above the sea level

MED Minimum Erythral Dose

NIR Near Infrared

Okta Unit used in meteorology to describe the amount of cloud cover at any given location

s Second

SZA Solar Zenith Angle

UV Ultraviolet radiation

UVA Ultraviolet A

UVB Ultraviolet B

UVI Ultraviolet index

W Watt

WHO World Health Organization

λ Wavelength

Introduction

There is currently a great deal of interest in using photoactive materials which absorb energy to give rise interesting electrical, optical and chemical properties that can have a wide range of applications as outlined by [Nakata and Fujishima \(2012\)](#). Solar radiation can be a free and naturally available source of photons to excite these materials. Solar radiation is the most omnipotent direct source of energy in the earth and, as such, is of tremendous importance for secondary and tertiary sources of energy and conversion. [Escobedo et al. \(2011\)](#) reported that the most intense part of the spectrum of solar radiation is broadly divided into three portions: the ultraviolet, UV (~between 290 and 400 nm), visible, vis (~between 400 and 700 nm), and near infrared, NIR (~ between 700 and 2500). Many of these photoactive materials absorb part of the solar spectra most of which falls within the UV range.

An estimation of the terrestrial availability of UV radiation is important in designing solar panels, many cosmetic and health products, agriculture and environment using such UV-active materials. It is also important with respect to the design and

performance of photoactive materials that are sensitive or responsive to any of the above ranges or a particular wavelength within these ranges of solar radiation. The attenuation of solar radiation in the UV range at different levels of the atmosphere and terrestrial conditions significantly affects the activity of photo-responsive materials used in a range of applications including Dye sensitized solar cells (DSSC), UV shielding, and photocatalysis based antimicrobial surfaces. There are number of commercial solar simulators and software tools available for measuring performance of DSSC in simulated solar conditions. These products generally emphasize on the full solar spectra including part of the UV that can be available, e.g., in the roof top or large area exposed to sun for photovoltaic storage. The dosage of energy required to excite a photo-responsive material plays an important role in photocatalytic performance and as such important for photo-sterilization applications as outlined by Escobedo *et al.* (2011).

Photocatalysts responsive to the solar spectra produce photochemical reactions that have been used for, e.g., self-cleaning glass as reported by Ahmed *et al.* (2016) and Sakhuja *et al.* (2014) and can also be used for self-sterilization (Tofail *et al.*, 2012; Kowal *et al.*, 2016). The energy dosages required for terrestrial antimicrobial effects are not readily available, however. This makes a rational interpretation of the in vitro data obtained under in situ simulated conditions difficult to link to their expected operational performance in the ambient. This absence blurs the minimalistic design approach as regards to the amount of photocatalysts to be used to make a surface photo-sterilizing based on the minimal inhibitory concentrations found from in vitro experiments. That many photocatalysts are most effective in their nanoscale dimensions which may give rise to nanotoxicity and occupational hazard is another issue that must be addressed so that the design of photo-sensitive surfaces using nano-size photocatalysts do not give rise to health and environmental concerns during the production and product life-cycle as reported by Mullins *et al.* (2013).

Background/Fundamentals

Fundamentally, the UV dosage depends on the effective wavelength (λ), the intensity of radiation described as radiance (E), and the duration of irradiation (h). Due to the wide variation of terrestrial conditions due to geographic locations, seasonal changes, cloud, forest and vegetation it is difficult to obtain a single value that can be used as a benchmark for available solar conditions in a given place where a photocatalyst containing product would function. The challenge of establishing any reference values of solar radiance across different geographical location over different times of a day (or night) is not trivial. Different segments of the solar radiation attenuate differently on the path to the surface of the Earth. The Earth surface also reflects some parts of the incoming radiation. For example, shorter wavelength radiations of the UV are typically absorbed by the stratosphere and do not reach the Earth Surface as reported by Urban *et al.* (2016).

According to Silva Porfirio *et al.* (2012) The solar ultraviolet spectrum (280–400 nm) is divided into 3 main parts. The UVA (320–400 nm) or the near UV region consists of the wavelengths to which stratospheric ozone is transparent. It is used by human body in synthesis of vitamin D and responsible for sun tanning but also can cause premature aging of skin. The UVB (280–320 nm) or the erythral region can cause skin burn and changes in immunological system including skin cancer (Mead, 2008) and eye diseases such as cataract. The UVC (100–280 nm) region is highly energized radiation. It is harmful to life but does not reach the surface due to absorption by the stratosphere. The ultraviolet radiation components UVA and UVB make less than 10% of a global solar radiation spectrum (Navntoft *et al.*, 2012) and UVA is mostly 90%–95% of UV (Diffey, 2002). Only UVA and UVB are relevant for terrestrial applications.

The radiant exposure causing redness of the skin is described as the Minimum Erythral Dose (MED, Jm^{-2}). Due to the potential harmful impact of UV light on human a linear scale for dosage is recommended by the World Health Organization (WHO) to indicate the risk of potential sunburn. This linear scale, known as the UV index (UVI), represents the intensity of sunlight that can cause sunburn of skin over a defined period of time. The UVI value is determined from the amount of radiation in the spectral range, typically between 280 and 400 nm including both UVB and UVA, in which light interacts with skin. Kudish *et al.* (2005) and the WHO (2014) outlined that One unit of UVI represents an exposure to the radiation equivalent to the energy of 25 mWm^{-2} . This parameter is commonly used in meteorology and is presented in weather forecasts as regards to corresponding risk levels posed by the ultraviolet radiation. The UVI ranges from a scale of 1 (lowest risk) to 11 (highest risk). The UVI is the greatest when the Sun reaches its highest point around noon representing the shortest path length towards the terrestrial exposure and hence the least attenuation of cancer causing UVB. UVI varies across the World due to its slightly oblate spherical shape, a slant between the Earth's axis and its orbit around the sun and the changes in season. Sharma *et al.* (2012) reported that areas that are on the equatorial latitude (20°S – 30°N) are generally shows the most extreme cases of UVI generally in July when the Sun is at the zenith. While UVI is widely used, in particular in MED dosimetry for UVB causing skin cancers, very little insights can be obtained readily from UVI to derive values that are useful for predicting or assessing photocatalyst performance involving UVA region in the solar spectra.

As 90%–95% of the terrestrial UV radiation is actually UVA, the UVI is not a good measure for terrestrial availability of UVA. Here we review and harmonize literature data on the “availability” of UVA radiation across a few selected geographical locations at different times of a day in a year. We also conduct experiment on the availability of UV under different conditions in Ireland, a country known for its low solar availability due to the altitude as well as the Atlantic conditions. The conditions for Ireland can be taken as the nearly worst case scenario of the availability of solar UV radiation for conversion by photoactive materials from natural sunlight. The study allows us to obtain, for the first time, a general guideline of the terrestrial availability of UVA radiation to estimate the minimum and maximum value of UVA radiance that can be used to benchmark the performance of materials active

Table 1 Short compendium of parameters used in radiometry

<i>Objective radiometry parameters</i>			
	<i>Physical quantity</i>	<i>Equation</i>	<i>Unit</i>
1	Radiant energy – energy of electromagnetic radiation	Q_e	(J)
2	Radiant flux – radiant power, energy radiated in unit time	$\phi_e = \frac{dQ_e}{dt}$	(W) or (J s ⁻¹)
3	Irradiance – power density, radiant flux density	$E = \frac{\phi_e}{A}$	(W m ⁻²)
4	Radiant exposure – accumulated energy per area	$GE = \sum E$	(J m ⁻²)
5	Dose of delivered energy in time	$D = E \cdot t$	(J m ⁻²)

in this region. This general guideline will be highly useful in photocatalysis design and validation under simulated solar UV conditions leading to performance prediction of products when working in natural light.

Parameters and Units Used in Radiometry

Here several parameters from radiometry are discussed. All of them are used in the discussed subject to describe the relationship between energy of light, surface and time. Most frequently used parameters are presented in [Table 1](#). Energy of light, which in the discussed application we can relate to the energy emitted by Sun is described as Radiant energy. Radiant flux refers to the amount of energy that radiates in the unit of time. Irradiance tells us how much of the radiant flux is received on the surface: in particular case of UV studies irradiance reflects amount of UV received on the ground. Irradiance can be measured within the range of source wavelength (Spectral Irradiance) or at effective wavelength. Radiant exposure is a parameter describing amount of radiant energy received on the area (i.e., Energy of Sunlight accumulated on the surface). The amount of energy delivered is called as dose of energy. Values can be converted, if additional variables are known (i.e., time, surface area).

Light Sources Used in Excitation of Photocatalysts

Over the last decades many studies on nano-photocatalysts have been published, but as we have observed UV-light sources and their reported parameters varied. Here we are giving just few examples of the [Douki et al. \(2003\)](#) have been studying photo-products in genotoxic effect of Solar UVA Radiation. [Kuluncsics et al. \(1997\)](#) carried out an experiment, where cells were irradiated with UVA light where fluence rate equal to 1 kJm⁻²s⁻¹ corresponding to 1–5 h exposure to natural sunlight in Paris, at zenith, in summer. [Hessler et al. \(2012\)](#) analyzed interaction between P25 TiO₂ nanoparticles and planktonic bacteria. Stock solution of P25 was prepared and added to *Pseudomonas aeruginosa* inoculum. For the membrane integrity tests 8 W 365 nm Lamps (EN-180, Spectroline) were used and the intensity at a distance of 10 cm was 1.8 mWcm⁻² (18 Wm⁻²), which according to [Arimoto-Kobayashi et al. \(2002\)](#) studies falls in the range of UVA intensity found in natural light. The same value of radiance (18 Wm⁻²), was applied in research by [Appavoo et al. \(2014\)](#) on nanocomposite research. In the cited [Arimoto-Kobayashi et al. \(2010\)](#) short communicate intensity of solar UVA was 4.94 Wm⁻² at 360 nm, and 4.3–5.4 Wm⁻² intensity range was used by the group also in further research. [Fahlman and Krol \(2009\)](#) have investigated potential application of quercetin in skin protection against UV radiation. To simulate natural lighting products of quercetin were exposed to 7.4 Wm⁻² (740 μWcm⁻²) UVA radiance. [Duran et al. \(2012\)](#) studied the operation costs of treating a real effluent from power station in Spain. They have compared the photocatalytic process using different types of radiation- artificial UV or solar UV. Optimal conditions of the solar process were defined as 32.3 Wm⁻² average irradiation in the complete experiment. These discrepancies in UV radiance have drawn our attention to availability of UV light reaching Earth, as radiance significantly impact outcome properties of photocatalytic materials.

Significance of UVA Radiation in Photocatalytic Research

Activity of TiO₂ nanoparticles (P25 Aeroxide, Evonik) against Methicillin Resistant *Staphylococcus aureus* (MRSA) has been reported in our previous research: [Kowal et al. \(2011, 2014\)](#). We have studied antimicrobial activity of this material at low energy irradiance: 1–5 Wm⁻². Samples were irradiated using UVA lamp with maximum irradiance at 365 nm. Results are presented in [Fig. 1](#). An increase in antimicrobial effect was observed with amplification of light irradiance. After 2 h 50% of MRSA colonies were killed at 1 Wm⁻², whereas when UV radiance was higher no bacteria growth was observed. [Rodriguez et al. \(2014\)](#) have studied antimicrobial activity of photocatalytic textiles varying the power of UVA lamp 10–40 Wm⁻² as representing solar energy available in France. In the presented results authors have shown that antimicrobial activity of polyester fabrics coated with Titanium dioxide (P25, Aeroxide, Evonik) against *Staphylococcus epidermidis* increases with irradiance, whereas no antimicrobial activity was observed when irradiance was lower than 23 Wm⁻².

Dose of delivered energy plays an important role in photocatalytic research. There are three main variables: effective wavelengths of light source, intensity of source (radiance) and duration of irradiance. As presented in the introduction, UV sources that

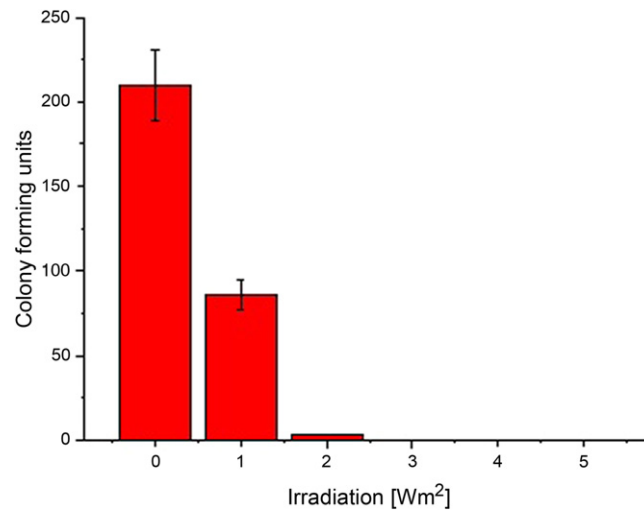


Fig. 1 Activity of titanium dioxide (P25, Aeroxide, Evonik) against MRSA under UVA irradiation at different irradiance.

are about to mimic availability of this range in sunlight differ from each other. Here, we also indicate that irradiance of applied light has a significant impact on experimental results. Reported availability of sunlight was then extensively studied to estimate its value in further research.

Factors Affecting the Terrestrial Availability of UV Radiation

Solar elevation

Navntoft *et al.* (2012) pointed out that the solar altitude depends on the time of day, day of year, and geographical location (latitude and longitude). The intensity changes with increase of the solar zenith angle; the number of UV rays emitted by the sun into a given solid angle is distributed over a larger area on the earth's surface. As the sun falls lower in the sky, the path length of the sun's UV rays through the atmosphere increases and as a consequence the intensity of UV reaching the Earth's surface decreases at all wavelengths, particularly those shorter than 320 nm. Parameters including location, season, time of the day are discussed in detail in subsections below.

According to the results given by Escobedo *et al.* (2011) UV radiation fraction is about 4% of global solar radiation and one of the parameters effecting UV spectral component is concentration of aerosol in air, which depends on the humidity of the environment.

Location: Coordinates, altitude

Amount of natural UV radiation available in the certain location depends on the actual coordinates of the area. The angle between zenith and the center of the Sun is called Solar Zenith Angle (SZA). Due to the curvature of the Earth, the shortest distance between Sun and Globe is on the Equator ($SZA = 90^\circ$), resulting in highest Radiance flux around 0° latitude. Perez-Burgos *et al.* (2015) report that irradiance reaching earth surface 60 Wm^{-2} at high latitude and 250 Wm^{-2} at low latitude. The trend of the decreasing daily flux with increasing latitude can be observed in data from Table 2.

The lowest irradiance can be expected at the North and South Pole. Lee *et al.* (2015) have published data from King Sejong Station on King George Island (Antarctica), showing that the mean UV_{near} varied from 35 Wm^{-2} at $SZA = 50^\circ$ to 10 Wm^{-2} , when $SZA = 75^\circ$ under clear sky conditions. As outlined by Diffey (2002) the distance between Earth and Sun varies due to elliptical orbit of the sun. This results in variation of UV intensity between Southern and Northern Hemisphere. According to the data

Table 2 Example of UVA daily flux values in the locations in winter time: Daily flux decreased with the increase of the latitude

Location			Weather details	UVA daily flux		Sources
				Reported data In various units	Harmonized data (kJ m^{-2})	
Country	City	Coordinates				
Austria	Innsbruck	47°N 11°E	Winter	$0.24 (\text{MJ m}^{-2} \text{ day}^{-1})$	240	Blumthaler <i>et al.</i> (1997)
Cyprus	Athalassa	35°N 33°E	December	$245 \pm 40 (\text{kJ m}^{-2})$	245 ± 40	Jacovides <i>et al.</i> (2009)
China	Heshan	22°N 112°E	March	$346 (\text{kJ m}^{-2})$	346	Gong <i>et al.</i> (2015)

presented in the paper as a reference spectrum measured on a clear summer's day around noon at $\lambda = 365$ nm, spectral irradiance $G = 0.683 \text{ Wm}^{-2} \text{ nm}^{-1}$ in Albuquerque ($38^\circ\text{N } 106^\circ\text{W}$) and $G = 0.766 \text{ Wm}^{-2} \text{ nm}^{-1}$ in Melbourne ($38^\circ\text{S } 145^\circ\text{E}$). Total irradiance in UV range was 52 Wm^{-2} on Northern Hemisphere (38°N) and 61.5 Wm^{-2} on Southern (38°S).

Altitude has an impact on the radiant flux, as well. Blumthaler *et al.* (1997) examined the increase in solar radiation with altitude over 2 month's periods so that all seasons of the year were covered at each station. Stations in Jungfraujoch (Switzerland) and Innsbruck (Austria) are separated by 270 km. Under clear sky conditions, the observed increases in irradiance with altitude (altitude effect) of the daily totals of global irradiance were $8 \pm 2\%$ per 1000 m (total irradiance), $9\% \pm 2\%$ per 1000 m (UVA irradiance) and $18\% \pm 2\%$ per 1000 m (erythral effective irradiance) during the summer. The altitude effect of the simultaneously measured erythral effective irradiance between Innsbruck (577 m a.s.l.) and Hafelekar (2300 m a.s.l.), horizontally separated by 2.5 km, suggests a solar elevation dependence: $15.1\% \pm 1.8\%$ per 1000 m at 60° solar elevation and $18.6\% \pm 2.9\%$ per 1000 m at 20° solar elevation. Simultaneously taken measurements of solar irradiance with high resolution spectrometers at Garmisch-Partenkirchen, Germany (730 m a.s.l.) and Wapik (1730 m a.s.l.), horizontally separated by 5 km, indicate a wavelength dependence of the altitude effect on the global irradiance: 9% per 1000 m at 370 nm increasing to 11% per 1000 m at 320 nm and 24% per 1000 m at 300 nm.

Time of a day

Diffey was analyzing summer spectral irradiance at noon on clear days.¹² The sun's UV rays are strongest in the 4 h period around local noon when 50%–60% of a summer's day UV is received. The author claims that about 9% of solar radiation is UV, but this value varies with solar rotation and cycle of sunspot activity.

The distribution of UV light throughout a clear summer's day in the United Kingdom was also studied. UVA radiance reaches 45 Wm^{-2} at noon. According to the author, the highest percentage of ambient UV during a clear summer's day is the highest between 12:30PM–1:30PM and reaches 17% of daily UV. Availability of UV light is the lowest in the evening (after 6:30PM), only 1% of diurnal received radiation.

Months and Seasons

Jacovides *et al.* (2009, 2012) have measured global UVA radiant fluxes in the eastern Mediterranean basin, hourly in Athalassa, Cyprus from 1st January 2004–31st December 2006. The hourly radiometric data used in this analysis were collected at the semi-urban Athalassa site, located in the central low-lying area of Cyprus; Mediterranean climate characterized by a succession of one rainy season (November–February) and one long dry season (March–October). Moreover, from late summer through September during the early afternoon hours, Athalassa is affected by the prevailing wet westerly winds blowing from Morphou Bay increasing thus atmospheric moisture content.

They daily UVA in December equals $\text{Guva} 245 \pm 40 \text{ kJm}^{-2}$, and July daily $\text{Guva} = 790 \pm 50 \text{ kJm}^{-2}$. These observations correspond to results presented by Diffey (2002) the highest doses of UVA are received in June – July, and lowest in winter: December and January. In 2012 they have published data recorded in 2006 during solar eclipse at Acropolis – Radiant flux dropped to 0 Wm^{-2} at 11:00 am, and the maximum hourly radiation of UVA that particular day was 18 Wm^{-2} after eclipse ending.

In papers by Kudish and Evseev (2000, 2014) average daily irradiances were measured annually in Israel. The radiation was monitored at two meteorological stations: one located in the Dead Sea basin at Neve Zohar; and the other in Beer Sheva. Neve Zohar is situated in the Judean desert and is on the western shore of the Dead Sea. Beer Sheva is located in the southern Negev region of Israel, a semi-arid zone, at a distance of 65 km to the west of the Dead Sea and situated at 315 m above mean sea level. The UVA measurements were initiated at Neve Zohar in February 1995 and the radiation has been monitored continuously. In the paper published in 2000 average daily irradiances were 259.01 Wm^{-2} in Neve Zohar and 269.33 Wm^{-2} in Beer Sheva. In 2014 the same group has published the 18 years irradiance data and daily values for Beer Sheva. The highest daily irradiances were observed in June and average value was 399.78 Wm^{-2} , and the lowest irradiance recorded in December was 135.52 Wm^{-2} .

Navntoft *et al.* analyzed solar UV radiation in Spain.¹¹ Solar UV radiation was measured over 4 years on tilted and horizontal planes located at the Plataforma Solar de Almería, Spain. The monthly mean ratio of tilted/horizontal solar UV irradiation varies with the time of the year, reaching values of 1.25 and 0.95 for winter and summer, respectively.

Noted values of monthly mean global UV diffuse irradiation were the highest in July (7629.11 Whm^{-2}) and the lowest in December (2231.91 Whm^{-2}), from those values hourly UV radiation equal 10.6 Wm^{-2} in July and 3.1 Wm^{-2} in December. The highest UVA irradiance was recorded in August and reached 45 Wm^{-2} . Also they have reported higher UV energy received at tilted surface: 3%–4% more at 37° inclined plane than the horizontal plane.

Ruiz-Arias *et al.* (2015) conducted analysis of the data collected from 10 years in Spain. They observed a gradient: lower values of irradiation northward. Results obtained in winter months were more homogenous, higher variability was observed in summer time, due to local cloudiness. It was reported that mountains form a natural barrier for northern winds, forcing orographic lift of masses of humid air from the sea which rise to form local clouds.

Atmospheric attenuation (pollution) changes over years, urban, rural

Gong *et al.* (2015) estimated amount of UV in China. Authors noted that aerosol's loading has significantly increased over last year's due to economic development and urbanization. Aerosols disperse solar radiation more in UV range than in full spectra, as extinction effect of aerosol decreases with wavelength. Location-based distribution of UV was also studied as annual average of UV

in Heshan (Pearl River Delta region in China) is higher than in Beijing or Wuhan (which are situated northern to Heshan) and lower than in Lhasa (southern to Heshan) [Gong et al. \(2015\)](#) and [Wang et al. \(2013\)](#).

Clouds

Clouds have fundamental role in attenuating solar radiation reaching Earth. Clouds are measured in oktas, which is a unit describing coverage of the sky: number of eights of the sky covered in cloud, where 0 oktas refers to a clear sky and 8 oktas is overcast. Unlike location, the structure and composition of clouds is unpredictable and constantly alternating. Most papers report data obtained at clear days, as estimation of UV radiance on overcast day is very difficult, hence as reported by [Serrano et al. \(2015\)](#) it can attenuate even up to 80% of solar radiation comparing to the clear sky. The impact of clouds reflects amount of clouds, cloud type and height and cloud optical depth. The parameter used to define impact of clouds on UVA radiation is Cloud Modification Factor (CMF_{UVA}), which is defined as follows:

$$CMF_{UVA} = \frac{UVA_{cloudy\ sky}}{UVA_{clear\ sky}} \quad (1)$$

It reflects the ratio between UVA radiations on cloudy days to clear days. The CMF can be applied to global radiation (CMF_{global}), UVB radiation (CMF_{UVB}), UVA, etc., as long as wavelength range is the same in both variables. Amount of clouds has a direct impact on UVA – the dose decreases with increase of cloud amount. [Feister et al. \(2015\)](#) report that minimum and maximum cloud modification factors of UVA at Lindenberg (47°36'N 09°54', 878 m a.s.l.): 0.350–1.153 in July 2014, 0.010–1.337 (min – max respectively) in August 2014. They also report maximum extraterrestrial UVA and model values of UVA as 90 Wm^{-2} and 80 Wm^{-2} respectively at Licancabur volcano in Chile/Bolivia (22°50'S 67°52'W, 5920 m a.s.l.).

Influence of clouds is determined by type, amount, height, optical depth of the clouds. Cirrus clouds have low optical depth, they are regionally endemic, can influence spectral optical properties of aerosol as studied by [Chew et al. \(2011\)](#). [Aun et al. \(2011\)](#) report that the influence of the clouds varies with wavelength- attenuation increases with wavelength. The influence of clouds on daily exposures to UVA was studied by [Parisi et al. \(2014\)](#). Exposure of UVA decreases with solar zenith angle and increase of cloud cover. From their research it may vary from 47 Wm^{-2} to 3 Wm^{-2} when the sky is covered. Reported CMF_{UVA} values change from 0.97 (1 okta) to 0.50 (8 oktas) and CMF_{global} from 0.90 (1 okta) to 0.40 (8 oktas).

[Silva Porfirio et al. \(2012\)](#) assessed global UV solar radiation under various sky conditions in the eastern coast of Northeast Brazil, at the Rio Largo County (25 km from the coast) considered part of the metropolitan area Maceió, capital of Alagoas State in Brazil. The global and UV solar radiation measurements were taken at the agro-meteorological/radiometric station (9°28'S, 35°49'W, 127 m of altitude) located at the Center for Agricultural Sciences of the Federal University of Alagoas. This tropical region has a climate classified as megathermal or humid tropical, with a rainfall concentration during autumn to winter (March to August). The maximum of UV solar irradiance was observed around local noon, under clear and partially cloudy sky, where the maximum of solar UV irradiance under clear sky conditions are practically constant for global solar irradiance levels above 1000 Wm^{-2} (for the dry period) and 800 Wm^{-2} (for the rainy period). During cloudy days multi reflection occurs and increases of up to 18.8% in UV solar irradiance and 14.9% in global solar irradiance in comparison to clear days. The maximum value of the daily UV dose was 0.85 MJm^{-2} , with an annual average of 0.55 MJm^{-2} . The analysis indicated that daily UV irradiation variability is influenced more by the cloudiness than seasonal factors. The hourly monthly UV irradiance was similar to the global irradiance throughout the year, where the highest observed during Spring/Summer months (dry period) and lowest during Autumn/Winter months (rainy period), which correspond to before mentioned research.

[Lee et al. \(2015\)](#) report that UV radiation can be enhanced under broken cloud conditions due to reflections from clouds. Their observations in western Antarctica indicate that total ozone has a significant impact of UV within erythemal region (280–320 nm), but in near UV (295–385 nm) radiation is sensitive to cloudiness. The transmittance through atmospheric layer is higher in that range, than the other. They also claim that UV radiation in near UV is less sensitive to variation of SZA than in case of UV.

Surface reflection

Reflection of solar UV radiation from most ground surfaces is normally less than 10%. Gypsum sand reflects about 15%–30%, snow can reflect up to 90%, calm water reflects only about 5% of incident UV radiation; up to 20% is reflected from choppy water. According to [Lee et al. \(2015\)](#) now cover increases UV radiation 9%–17% on partially cloudy days and 6%–50% at overcast days.

Diffey was analyzing summer spectral irradiance at noon on clear days. The sun's UV rays are strongest in the 4 h period around local noon when 50%–60% of a summer's day UV is received. The author claims that about 9% of solar radiation is UV, but this value varies with solar rotation and cycle of sunspot activity. Also the distance between Earth and Sun varies due to elliptical orbit of the sun. This results in variation of UV intensity between Southern and Northern Hemisphere.

Current Models Describing UV Availability

[Angstrom \(1924\)](#) introduced model estimating global solar radiation using sunshine hours. The model relates monthly average daily global radiation to the average daily sunshine radiation through number of sunshine hours and maximum number of sunshine hours in a ratio of regression coefficients. [Hargreaves and Samani \(1982\)](#) recommended an equation including mean

daily temperature amplitude, extraterrestrial radiation multiplied by empirical coefficient. Since then the estimation tools have become more complex, utilizing technologies, resulting in more adequate models.

Navntoft *et al.* (2012) have used a theoretical model to estimate solar radiation (TUV 4.1). Model uses following parameters: scattering due to gases ($N_2 + O_2$), ozone absorption (negligible at wavelengths higher than 320 nm), optical depth of ozone and air, aerosol concentration, heterogenic character of atmosphere (clouds, pollutants, ozone, aerosol). To calculate solar UV irradiance at a given horizontal surface on a clear day, the model requires following inputs:

- Geographical parameters: latitude, longitude, height above sea level,
- Time parameters: Year, month, day, hour,
- Atmospheric parameters: Aerosol optical depth, ozone concentration, and specific parameters (alpha wavelength coefficient and single scattering albedo).

Khahro *et al.* (2015) point out that evaluation of solar energy is also important for using renewable energy in solar panels, but there is no radiation data available for developing countries due to high costs. This is one of the drives to develop models, systems enabling estimation of global solar radiation on horizontal surface.

Most of the prediction methods is based on support vector regression (SVR), which bases on sunshine hours, maximum temperature, minimum temperature, average relative humidity and daily solar radiation (Piri *et al.*, 2015). Khahro *et al.* (2015) distinguish three main components of global radiation: diffuse radiation, beam radiation and ground reflected radiation. They were studying diffused solar radiation in Pakistan using 28 statistical models. The models present high accuracy. Estimated solar radiation in January was 26.37 and 45 MJm^{-2} in July. The values change with tilt angle.

According to Mohahammadi *et al.* (2015) who estimated global solar radiation in Isfahan, Iran SVR provides high level of accuracy in the field. The measured yearly average of solar radiation on horizontal level values was 19.47 MJm^{-2} .

Abukassem and Bero (2010, 2012) have been working on UV dosimetry and in their experiments UVA irradiation level was optimized to mimic natural solar UVA radiation level measured at mid-day during summer (21 June – 21 September 2008) in the Damascus region in Syria. The average value for solar UVA was about $60 \pm 5 \text{ Wm}^{-2}$. The intensity of UVA radiation beam generated at the laboratory was reduced to $58 \pm 3 \text{ Wm}^{-2}$ by applying UV neutral filters and according to the theoretical model and measurements irradiance values varied from 12 to 95 Wm^{-2} . For the research they have used 30 Wm^{-2} as representative irradiance value.

Piri and Kisi (2015) claim that models based on sunshine hours are more accurate than those based cloudiness and temperature. They have utilized models applying dynamic artificial intelligence, which use information about atmosphere thickness, available components in atmosphere. Their main conclusion was that emerging these type of models with Angstrom and Hargreaves-Samani equations can be successfully used in modeling solar radiation.

Norsang *et al.* (2009) estimated erythral dose of UVB in Lhasa, Tibet as 1.50 Wm^{-2} in January, below 2.5 Wm^{-2} in spring months, reaching 4 Wm^{-2} in during summer. The values obtained from measurement are correlating to the modeled values.

Estimation of UV Availability in Ireland

UV radiation in Ireland was measured in Limerick ($52^\circ 67'N$, $8^\circ 62'W$, 10 m a.s.l.) in April 2014 using Power and Energy meter PM 100D (Thorlabs, UK) equipped in Photodiode power sensor S120VC (Thorlabs, UK). The wavelength range for this particular sensor is 200–1100 nm (1 nm resolution), and 50 nW–50 mW power range.

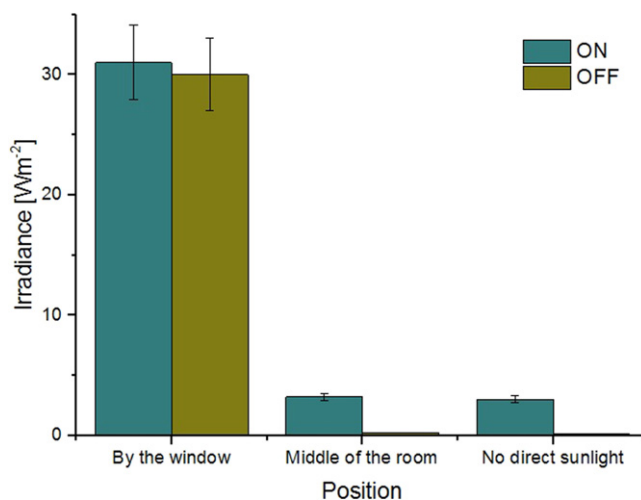


Fig. 2 Availability of UVA radiation indoors at three locations: by the window (majority of sunlight), middle of the room and in a room without windows (no direct sun light) with fluorescent lights turned on and off. Studies performed in April 2014 in Ireland, weather considered as sunny.

Measurements were taken in 3 different locations:

- Location 1 – room with windows, 3 m distance from the window.
- Location 2 – room with windows, measurements taken by the window.
- Location 3 – room without windows, no sunlight, only ambient light from the bulbs, height.

Measurements were taken when fluorescent lamps in the room were turned on and turned off to study input of indoors conditions on UV availability. Results are presented in Fig. 2. Maximum radiance was 30 Wm^{-2} . Interestingly, UV radiation was noted indoors, when sunlight was limited or not present at all. Radiance around 3 Wm^{-2} was available from fluorescent light bulbs, where the distance between light bulbs and measurement point was 1.8 m.

Harmonization of Literature Data

Radiation values taken from the literature have been converted to compare them between each other. Flux data are presented in Table 3, where radiation data are gathered in Table 4. Both tables reflect the indications from the literature studies. In Table 3 the UV flux is higher at lower latitude, increasing with altitude. Values obtained in winter are lower than flux in summer. Irradiance values change at different locations.

Maximum values presented in Table 4 indicate that UV irradiance in Europe are within $30\text{--}60 \text{ Wm}^{-2}$. Selection of UV light sources to mimic the natural conditions in current technologies should be considered with regards to the equivalents cited in the literature and weather conditions in the studied location.

Our study thus indicates that factors influencing the amount of UV light reaching the Earth can be divided into groups related to placing in time, location and climate conditions as outlined in Table 5.

Solar UV irradiance depends on several factors: geographical (location), meteorological (cloudiness), environmental (pollution), seasonal and an exact time of the day, when the measurement was taken.

Elementary factors that influence exposition of UV are:

- Position of the sun (depending on a day, hour, season) – solar irradiance is highest during summer, when the Sun reaches is highest point (around noon)
- Height above sea level – the highest the measurement station is, the greatest UVA irradiance
- Latitude – UVA irradiance is greater closer to the equator,

Table 3 Terrestrial availability of UVA light at different longitude, elevation

Location				Weather details	Type of measurement	Flux		Sources
Country	City	Coordinates	Altitude (m a.s.l.)			Reported data In various units	Harmonized data (kJ m^{-2})	
France	Paris	49°N 2.4°E	60–130	Sun in Zenith, summer	1–5 h to natural sunlight	1 ($\text{kJ m}^{-2} \text{ s}^{-1}$)	86,400	Douki <i>et al.</i> (2003)
Switzerland	Jungfrauoch	47°N 8°E	3576	Winter	Daily flux	0.32 ($\text{MJ m}^{-2} \text{ day}^{-1}$)	320	Blumthaler <i>et al.</i> (1997)
				Summer	Daily flux	1.89 ($\text{MJ m}^{-2} \text{ day}^{-1}$)	1890	
Austria	Innsbruck	47°N 11°E	577	Winter	Daily flux	0.24 ($\text{MJ m}^{-2} \text{ day}^{-1}$)	240	Blumthaler <i>et al.</i> (1997)
				Summer	Daily flux	1.48 ($\text{MJ m}^{-2} \text{ day}^{-1}$)	1480	
Cyprus	Athlassa	35°N 33°E	165	December	Daily	245 ± 40 (kJ m^{-2})	245 ± 40	Jacovides <i>et al.</i> (2012)
				July	Daily	790 ± 50 (kJ m^{-2})	790 ± 50	
China	Heshan Pearl River Delta Station	22°41'N, 112°54'E	56.4	March	Monthly mean UV	346 (kJ m^{-2})	346	Gong <i>et al.</i> (2015)
				July		856 (kJ m^{-2})	856	
Brazil	Maceió	9.7°S 36°W	127	Dry season	Daily UV irradiation	0.85 (MJ m^{-2})	850	Silva Porfirio <i>et al.</i> (2012)
Brazil	Botucatu	22°85S 48°45W	786	–	Maximum value	1.29 (MJ m^{-2})	1290	Escobedo <i>et al.</i> (2011)
				–	Minimum	0.04 (MJ m^{-2})	40	

Table 4 Example of irradiance values at different locations

Location				Weather details	Type of measurement	Reported data ($W\ m^{-2}$)	Sources
Country	City	Coordinates	Altitude (m a.s.l.)				
United Kingdom	Durham	54°N 1.33°W	100–120	Clear summer day (max at noon)	Max irradiance at noon	45	Diffey (2002)
Ireland	Limerick	52°67N 8°62W	10	April	Max irradiance spring	30	NA
USA	Albuquerque	38°N 106°W	1619	Noon clear day	Total radiance	51.95	Diffey (2002)
Spain	Almeria, Tabernas Desert	37°N 2°W	3458	Clear day in August	Max irradiance	45	Navntoft <i>et al.</i> (2012)
Cyprus	Acropolis Nicosia site	35°N 33°E	220	Eclipse day	Max irradiance	18	Jacovides <i>et al.</i> (2012)
Syria	Damascus	34°N 36°E	680	Clear day	Max irradiance	60	Abukassem and Bero (2010, 2012)
Australia	Toowoomba	27.6S 151.9E	693	Clear	Max irradiance	47	Parisi <i>et al.</i> (2014)
Australia	Melbourne	38°S 145°E	31	Noon clear day	Total radiance	61.48	Diffey (2002)

Table 5 Description of parameters having an impact of UV radiation

Group	Parameter	Impact on UV radiation
Time related	Season	The highest in June – July The lowest in January – December
	Time of the day	The highest around noon, With the Sun coming down, UV rays path through atmosphere increases and UV intensity decreases
Location related	Latitude	The highest at equator, UV irradiance decreases with increase of latitude
	Altitude (m a.s.l.)	9% UVA increase per 1000 m 18% UVB increase per 1000 m
Climate related	Tilt	More UV delivered to tilted plane
	Pollution and ozone	Scattering of UV radiation, higher at urbanized areas
	Cloudiness	Diffusion of UV light
	Aerosol	Scattering and absorption of UV radiation
	Reflection	Normally 10% Sand reflects 15%–30% Snow 90% Water 5%–20%

- Reflection of the sun rays from the Earth which can reach about 10%–15%
- Ozone – the ozone layer absorb pollutants which scatter sunlight
- Cloudiness – clouds reduce UV intensity, but also can cause reflection of light.

Future Directions

Discuss the potential developments and future directions in the area of the contribution here.

Conclusions

Harmonization of literature data on terrestrial availability of UV radiation is important for obtaining a quantitative guidance on the effectiveness of UV active photocatalysts used in biology and chemistry. Typical applications include solar panels, cosmetic and health products, agriculture and environment that utilized UV-active materials. Based on literature data and our own experimental observations we have endeavored in such harmonization using the linear scale for potential sunburn dosage, UVI to estimate

terrestrial availability of UVA for practical applications. We have elaborated a general guideline of the terrestrial availability of UVA radiation. This allows to set the minimum and maximum values of UVA radiance that can be used to benchmark the performance of UVA active materials and compare across different types of applications especially in performance prediction of products when working in natural light.

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Development in Materials for Manufacturing Electronics With 3D Printing

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Abstract

Three-dimensional (3D) printing or additive manufacturing (AM) appears to be one of the promising technologies with numerous advantages and innovative usages as it diminishes worldwide energy utilization and CO₂ releases related to manufacturing processes in industries. It is a manufacturing process utilized for fabricating a 3D product by adding layers from a 3D-model as required. The adoption of 3D printing (3DP) techniques and technologies, particularly for printed electronics, has the potential to revolutionize flexible electronics industry, and other fields. From a fundamental standpoint, every application must take into account the materials that are available, the speed of creation, and the resolution of 3DP techniques. This article offers a fundamental overview of 3DP techniques as well as the applications and classifications associated with this advanced technology. The most recent advancements in unique 3DP materials for fabricating electronic products have also been presented. Most importantly, this article emphasizes the significant role of 3DP in current research advancements, directing readers to concentrate on the current challenges faced by this technology and afterwards outlining future research outlooks to advance 3DP technology.

Key Points

- Presented a fundamental overview of 3D printing techniques, classifications and the applications
- Provided recent advancements in unique 3DP materials for fabricating electronic products.
- Identified key role of 3DP in current research advancements
- Acknowledged the current challenges faced by this technology and outlining future research outlooks

Introduction

Manufacturing is regarded as the foundation of any industrialized nation because it serves as a barometer for nation's citizens' standard of living and directly affects a nation's economic strength (Duflou *et al.*, 2012). Today's economic development, industrial and commercial applications, and technological and scientific advancement all depend greatly on the manufacturing technologies (Ghimire *et al.*, 2022). With the advancement of technology, fabrication technology has been transformed from conventional manufacturing to intelligent, sustainable, and highly efficient manufacturing to embrace the fourth industrial revolution or Industry 4.0 (Kumar, 2018; Mehrpouya *et al.*, 2019; Quanjin *et al.*, 2020). A number of drawbacks are associated with the traditional manufacturing processes like milling, welding, shaping, rolling, CNC machining, forming, and casting, including presence of residual stresses, high material waste, a high level of expertise needed, a lack of automation, high level of complexity, expensive machining, inventories and massive supply chains, design immobility, shipping, a lack of customization, and increased carbon emissions (Araujo *et al.*, 2015; Ingarao, 2017; Ahilan *et al.*, 2013; Saloniitis *et al.*, 2016). The procedure is relatively expensive because it requires a lot of equipment and produces a lot of wasted materials. It is considered to be unfriendly to the environment and requires multiple chemical processing steps. Completely designing and patterning each layer takes time and requires iteration (Shahrubudin *et al.*, 2019). These issues are considerably resolved by 3DP-based manufacturing, allowing the use of biodegradable and recyclable materials in creation, (Revilla-León *et al.*, 2020; Attaran, 2017). The term "3DP" refers to a procedure that joins materials to build things from 3D Computer-aided design (CAD) model data, often layer by layer, instead of subtractive manufacturing and formative manufacturing methodologies (Pessoa *et al.*, 2021).

Numerous institutions have been prompted to reevaluate their worldwide supply networks as a result of the confluence of recent geopolitical events and the COVID-19 outbreak (Miller *et al.*, 2022). Due to these circumstances, interest in reshoring electronics fabrication capacity and boosting the R&D required to support this sector. This backdrop offers the ideal opportunity to think about how 3D printed electrical components might fit into a newly imagined electronics ecosystem (Ibn-Mohammed *et al.*, 2021). Technology for AM, or 3DP, offers the benefits of customization, digitization, and personalization. Researchers are now making great progresses in the investigation of printable materials and the enhancement of printing precision in the field of 3DP. Over the past thirty years, additive manufacturing (AM) has undergone an astonishing amount of development (Thompson *et al.*, 2016). Many printing techniques were found over time, and in under three decades, the application of AM technology has been dramatically expanded, which changed the logistics and production processes (Stansbury and Idacavage, 2016). Significant efforts

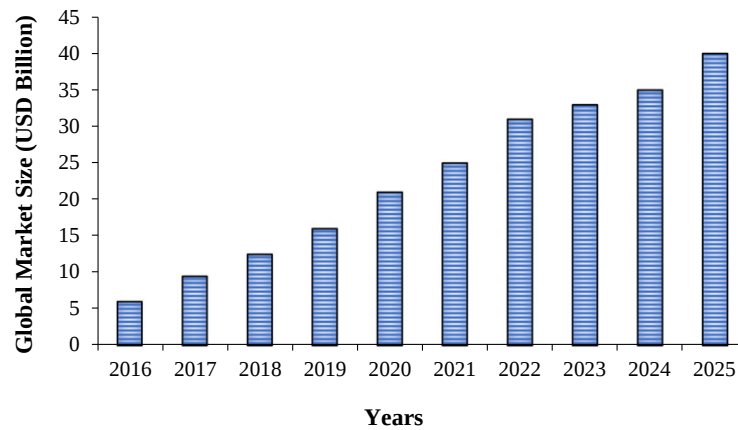


Fig. 1 The annual global market for 3DP. Adapted from Wang, Y., *et al.*, 2021. Applications of additive manufacturing (AM) in sustainable energy generation and battle against COVID-19 pandemic: The knowledge evolution of 3D printing. *J. Manuf. Syst.* 60, 709–733. Available at: <https://doi.org/10.1016/J.JMSY.2021.07.023>.

are being made by numerous nations to advance 3-D printing technology. China came in second with an 11% share of the publications total for 3DP research in 2020, with the United States contributing the majority (approximately 39% of the total) (Wang *et al.*, 2021). The global market for 3DP is expected to reach a value of roughly USD 40 billion by 2025 as shown in Fig. 1, based on the estimated annual growth rate of the market. Investments in AM technology have increased significantly, from USD 4 billion in 2014 to over USD 21 billion by 2020 (Thompson *et al.*, 2016).

Currently, 3DP is broadly utilized throughout the globe. In the fields of agriculture, healthcare, the automobile sector, and aerospace industries, 3DP technology is being used more and more for mass customization and manufacture of any types of open source designs (Ngo *et al.*, 2018; Yan *et al.*, 2018; Zou *et al.*, 2021; Singh *et al.*, 2020). The production line could shift and be revolutionized by 3DP technology. Utilizing 3DP technology will speed up production while cutting down costs (Gebler *et al.*, 2014). The consumer's demand will also have more of an impact on production at the same time. Customers might request that a product be created according to their specifications and have a greater say in the final result. In the meantime, 3D printing facilities will be situated nearer to the consumer, enabling a more adaptable and quick manufacturing process as well as improved quality control (Shahrubudin *et al.*, 2019). The objective of the researchers has been to actualize AM as an end-part production technique. Most contemporary electronic gadgets have printed circuit assemblies (PCAs), which are essential components and conventional term for electronic assembly assists to integrate electronic active, and/or passive elements, substrate and interconnections to obtain a wanted functionality. These components are composed of insulating, conductive, and semiconductor substances, among others. The requirement for multi-material 3DP would be a crucial condition when contemplating the use of 3DP in the fabrication of PCAs (Persad and Rocke, 2022).

This chapter's overall objective is to describe the fundamental ideas and challenges involved in electronics manufacturing and to overcome these difficulties electronics using new 3D printing methods and materials in building electronic elements, circuits, and gadgets. The current state of 3D printing is analyzed in order to assess its development potential and maturity level. Additionally, the pertinent applications and 3D printing's outlook for the future are examined. Section "3D Printing of Electronics" begins by outlining the fundamental concept of 3PD with significant applications, materials classifications, and recent progress. The current development of 3DP, as well as the significant bottlenecks and future possibilities are explored in Section "Current Challenges and Future Outlook". Important conclusions are drawn in Section "conclusions".

3D Printing of Electronics

Three-Dimensional Printing (3DP)

Building freeform topographical maps and photo sculptures from two-dimensional (2D) layers laid the groundwork for AM about 150 years ago (Zhai *et al.*, 2014). The first modern AM techniques were developed through research in the 1960s and 1970s, including photopolymerization in the late 1960s, (Wohlert and Gornet, 2016) powder fusion in 1972, (Ciraud, 1972) and sheet lamination in 1979 (Nakagawa, 1979). It came after developments in CAD and CA manufacturing (CAM), such as the early 1950s introduction of numerical control machine tools, the early 1960s introduction of computer graphics and CAD tools, the late 1960s introduction of CAD/CAM systems, and the early 1970s introduction of low-cost computer monitors (Pipes, 1982). Utilizing photochemical machining and dual laser beams, Wyn Swainson created the first 3D printing pattern and submitted a patent application in 1971 (Swainson, 1977). In 1986, Charles Hull used 3DP technique for the first time in the stereolithography (SLA) procedure (Su and Al'Aref, 2018). After Charles Hull unveiled the first 3DP technology in 1986, the manufacturing sector created a wide range of production techniques that have been used in a wide range of industries. Hull created and developed a 3DP method

Table 1 Consecutive development trends of 3DP

Year	Field of application	Researcher/Organization
1971	Development of the first shape concerning 3DP employing photochemical machining	Wyn Swainson (1977)
1972	Development of the powder fusion	Ciraud and Pierre Ciraud (1972)
1979	Development of the sheet lamination	Nakagawa Nakagawa (1979)
1986	Development of the first 3D system by stereolithography	Charles Hull Su and Al'Aref (2018)
1989	Electro-Optical System (EOS) development for 3D parts production utilizing metal-laser sintering	Hans Langer Khaing <i>et al.</i> (2001)
1992	First selective laser sintering printers	Carl Deckard West and Kuk (2016)
1992	AM method utilizing spraying of substances	James E. Beck Beck <i>et al.</i> (1992)
1998	AM method utilizing micro casting of substances	C. H. Amon and others Amon <i>et al.</i> (1998)
2004	Development of the dual transfer mode patents by EOS	Edson Costa Santos and others Santos <i>et al.</i> (2006)
2007	Development of the Darwin printer	Bowyer's team Horvath (2014)
2007	3DP in surgical planning	Massimo Robiony and others Robiony <i>et al.</i> (2007)
2009	Development of the Mendel printer	Bowyer's team Horvath (2014)
2013	First bio printed fully cellular liver tissue	Organovo Collin de l'Hortet <i>et al.</i> (2016)
2016-present	3D food printing, 3D energy storage etc.	(Pant <i>et al.</i> , 2022; Areir <i>et al.</i> , 2017)

and obtained the stereolithography (SLA) patent in 1986. Scott Crump received a patent for fused deposition modeling (FDM) in 1990 (Gross *et al.*, 2014). Since then, 3DP has advanced significantly. The adoption of new 3D printing techniques and technologies, particularly for printed electronics, has the potential to revolutionize various fields, including wireless communication, flexible electronic, solid-state display, effective battery, etc., (Espera *et al.*, 2019a). The development of 3DP in various sector has been presented in Table 1.

The traditional approach to modeling and creating electronics is subtractive in nature, with the basic technique being the selective removal of materials patterned from a master template (Tong, 2022). New fields of electronics production have been made possible by AM technologies, sometimes known as 3D printing. With the advent of multiple layer complex electronics and novel substrate geometries, inkjet and aerosol-based 2D printing, which was previously utilized to fabricate homogeneous structural electronics on flat surfaces, has become obsolete (Zhang *et al.*, 2020). Construction of parts using 3D printing techniques is quicker and more flexible than using traditional manufacturing processes (Medellin-Castillo and Zaragoza-Siqueiros, 2019). The ability for 3D printing to reuse and recycle plastics, and reduce emissions are some of the other environmentally friendly features (Nyika *et al.*, 2021), (Mikula *et al.*, 2021). The technique is also able to create designs with intricate and optimized geometries, which aid in creating components with superior strength/weight ratios and lighter weights (Srivastava *et al.*, 2018). Numerous advantages of 3D printing have been illustrated in Fig. 2.

In 3DP, CAD drawings of 3D objects are constructed layer by layer (LBL) until the entire product is finished. LBL is not the only method for 3DP, continuous liquid interface printing (CLIP) and particle replication in non-wetting templates (PRINT) have also been developed (Tumbleston *et al.*, 2015). By combining several materials to form a single structure, 3DP creates actual objects from digital files. A CAD file in a format suitable for 3DP tools is used for the construction. 3DP is perfectly suited to the various applications since it is research-based, creative, and quick-moving (Chen *et al.*, 2020). A 3D CAD model of the thing serves as the basis for the process of 3DP. The model is cross-sectionally divided into layers using a slicing software, saved as a computer file, and then transferred to the 3D printer. The part/product is then created using a 3D printer by spreading each layer carefully from the source the material. The process of building up layers of material on top of one another to produce 3D prints is quite similar to that of an inkjet printer. Fused deposition modeling (FDM) (Daminabo *et al.*, 2020), stereolithography (SLA) (Kafle *et al.*, 2021), selective laser melting or sintering (SLM) (Neng Zhang *et al.*, 2020; Padmakumar, 2020), and inkjet and polyjet printing (Wagner *et al.*, 2019) are some of the several 3D printing technologies. AM processes can be arranged into seven classes as shown in Fig. 3. The combination of more of these processes can provide a feasible tool to manufacture multi-functional electronic. Beyond prototype and full-scale mass production, 3D printing has the ability to produce scalable electronic models with higher resolution and faster manufacturing processes.

Applications of 3D Printing

The popularity of 3DP across a wide range of sectors such as the automotive, aerospace, medical, mechanical, electrical, electronics, and educational sectors, points to a change in manufacturing that has most recently also been observed in the building industry (Albar *et al.*, 2020).

3DP in healthcare

Over the past ten years, 3DP has become more accessible, and its use in medicine is expanding quickly (Shahrubudin *et al.*, 2019). As the demand for biocompatible, customized, and sterilizable parts are increasing in medical sector, the technological

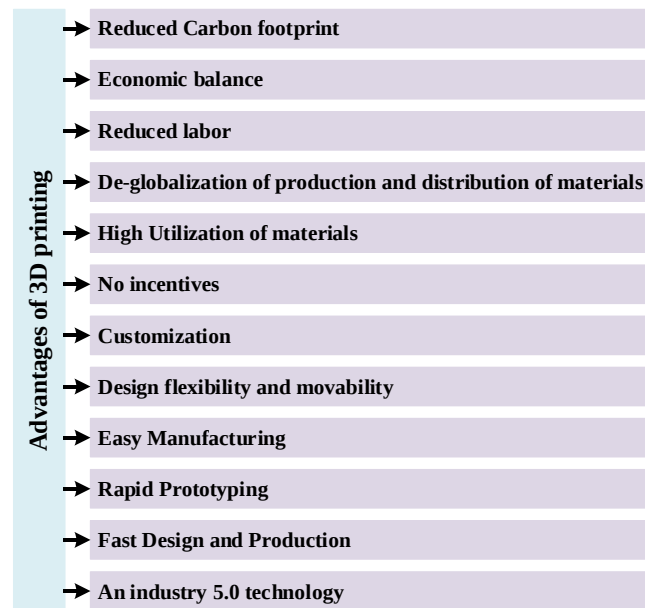


Fig. 2 Advantages of 3DP. Reproduced from Wang, Y., *et al.*, 2021. Applications of additive manufacturing (AM) in sustainable energy generation and battle against COVID-19 pandemic: The knowledge evolution of 3D printing. *J. Manuf. Syst.* 60, 709–733. Available at: <https://doi.org/10.1016/J.JMSY.2021.07.023>. Rodríguez-Reyna, S.L., Mata, C., Díaz-Aguilera, J.H., Acevedo-Parra, H.R., Tapia, F., 2022. Mechanical properties optimization for PLA, ABS and Nylon + CF manufactured by 3D FDM printing. *Mater. Today Commun.* 33, 104774. Available at: <https://doi.org/10.1016/J.MTCOMM.2022.104774>. Azlin, M.N.M., *et al.*, 2022. 3D printing and shaping polymers, composites, and nanocomposites: A review. *Polymer* 14 (1), 180. Available at: <https://doi.org/10.3390/POLYM14010180>.

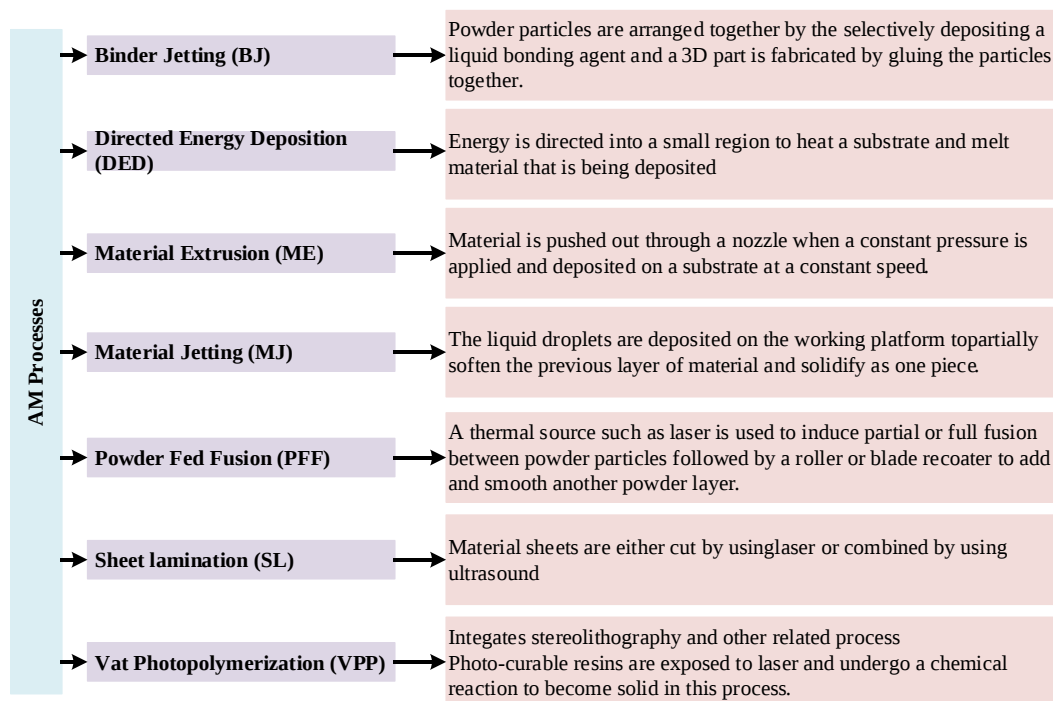


Fig. 3 Categorization of AM processes. Adapted from Lee, J.Y., An, J., Chua, C.K., 2017. Fundamentals and applications of 3D printing for novel materials. *Appl. Mater. Today* 7, 120–133. Available at: <https://doi.org/10.1016/J.APMT.2017.02.004>.

breakthrough of 3D printing offers numerous opportunities for study and development in the field of medicine. More hospitals are setting up 3D printing labs as affordable 3D printers and medical CAD software are becoming more readily accessible. By preparing for surgery with a 3D-printed model, surgeons can reduce the amount of time in the operating theater, leading to fewer

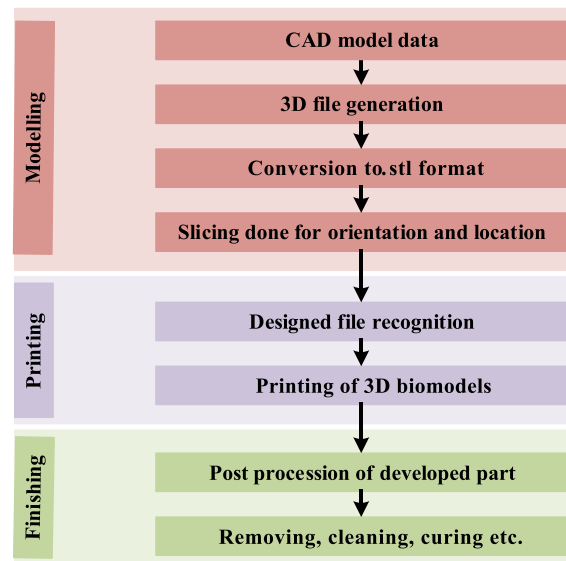


Fig. 4 Consecutive steps for realizing 3DP in healthcare.

issues and a better long-term prognosis for the patient (Manero *et al.*, 2019). The eight phases shown in Fig. 4 make up the basic and advanced processes for exploring 3DP applications in the healthcare field. The CAD model data serves as the foundation for creating the 3D file. It enables the user to create designed files in the .stl file format, which are then converted to G-code as necessary to create bio or medical parts as needed. The cutting is done to try and finalize the location and orientation of the selected portion. The desired bio-part or models must then be printed. The cleaning and curing processes can also be used to carry out the necessary post-processing stages (Yan *et al.*, 2018; Yadav and Sehrawat, 2019). There are various applications of 3DP in the field of healthcare as shown in fig. 4. In Chaudhuri *et al.* (2022), value creation, value proposition, value offered, and value capture to users by healthcare 3DP service providers was presented to determine the capabilities and resources that are necessary for the clinical group and the healthcare 3DP service givers to jointly create value.

Effects of 3DP in early-phase drug development, together with primary-stage human studies and pre-clinical research, and late-stage product fabrication were analyzed in (Tracy *et al.*, 2022). The benefits, state-of-the-art, and difficulties of using 3DP for mass production and customized dosing were introduced. There are many applications of 3DP in various sectors of healthcare such as drug or medicine, cost and efficiency, medical equipment, surgery-related, synthetic organs, basic medicine as illustrated in Fig. 5.

3DP in food printing

A rapidly developing technology, 3D food printing (3DFP) allows for customization in terms of flavor, texture, shape, and nutrition. Using 3DFP, it is possible to make innovative and beautiful versions of common dishes (Pant *et al.*, 2022). Patients with Dysphagia, or trouble swallowing are typically given timbales, which are modified puree-like foods with altered textures for ease of swallowing (Cichero *et al.*, 2013). Timbale's unique properties cause it to only faintly resemble the original ingredients, which decreases appetite, decreases nutrient intake, and even causes malnutrition. By creating more realistic and esthetically beautiful food, 3DP of timbales has the potential to improve the quality of life for patients with dysphagia and prevent undernourishment (Nopparat and Motte, 2022). Three processes are used to create 3DFP: 3D model creation, object printing, and post-treatment (Baiano, 2020). In (Liu *et al.*, 2020), the viability of 3D printing rice paste (japonica rice, waxy rice, indica rice), as well as the effects of sodium alginate (SA) added at various concentrations on the physicochemical and structural properties of rice paste (0, 0.25%, 0.50%, 0.75%, and 1.00%, w/w, dry rice flour basis) was examined. Fig. 6 illustrates the technique of 3DFP (Mantihal *et al.*, 2020).

The outcomes demonstrated that rice paste mixed with SA exhibited shear-thinning behavior, making it a perfect medium for 3DP. 3DFP can be utilized to successfully combat food waste from various sources. In Wong *et al.*, 2022, it have been shown that jackfruit seeds, which are frequently wasted and misused, may be printed in 3D. Food ink suitable for 3DP was created by boiling the trash using straightforward methods. In order to assist business owners and academics in the sector to focus their research and development (R&D) efforts, the business prospects of 3DFP was updated in Jayaprakash *et al.* (2020). In order to understand the perspectives of industry professionals, researchers, and potential customers, a three-phase mixed methods approach was used. Different diameters of wheat and rice fiber obtained from agricultural waste were combined with a photocurable resin for the first time in Romero-Ocaña *et al.* (2022) in order to fabricate a composite using stereolithography AM.

3DP in energy storage

Recently, there has been a lot of interest in the creation of porous 3D monoliths made of natural materials for a variety of purposes (Areir *et al.*, 2017). A range of 3D customized monoliths with high shape fidelity are produced using the substance extrusion-based

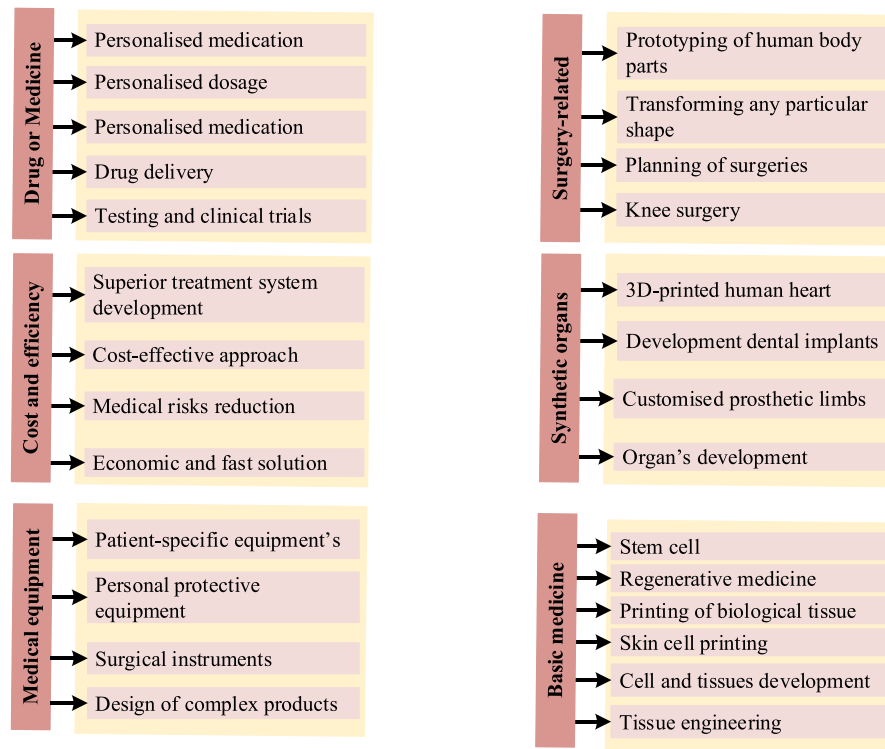


Fig. 5 Applications of 3DP in healthcare. Reproduced from Javaid, M., Haleem, A., Singh, R.P., Suman, R., 2022. 3D printing applications for healthcare research and development. Glob. Heal. J. Available at: <https://doi.org/10.1016/J.GLOHJ.2022.11.001>. In press.



Fig. 6 3D Food Printing process.

3DP technology and are useful for thermal insulation and energy storage (ES) applications (Zhou *et al.*, 2022). In Yang *et al.* (2023), machine learning (ML) was utilized to fully understand how the performance of supercapacitors (SCs) is influenced by typical structural features of 3DP electrodes consisting of graphene and carbon nanotubes. The temperature regulation of the star sensor baffle was addressed using a combination of 3DP and thermal ES technology in Guo *et al.* (2021). Tetradecane was selected as the PCM for heat storage, and the baffle body was 3D printed using aluminum with a lattice structure. The feasibility and effectiveness of combining 3DP with thermal ES technology for the temperature regulation of star sensor baffles in space applications were proven experimentally in this work. In Ghosh *et al.* (2022), a catalytically active material, conductive fillers, and polymer-based electrocatalytically active filament was created for FDM 3DP. By carefully adjusting the ratio of needed active material, such as other 2D materials, to desired polymers and conductive fillers, the optimized filament production techniques minimize the difficult fabrication of electrodes.

3DP in aerospace

The primary drivers of AM's exponential growth are its many advantages over traditional manufacturing processes, including its great cost effectiveness, reduced material waste, extremely high levels of freedom, and less material limits. The aerospace sector is one of the main drivers of this expansion (Madhavadas *et al.*, 2022). The adoption of this technology, historical and projected global aerospace AM market trends, and the effects of the Covid-19 pandemic on the current state of the global aerospace sector were all covered in Altuparmak and Xiao (2021). In Dagkolu *et al.* (2021), the design process for vital aircraft components used in fatigue-sensitive AM was outlined. A specific aerospace component that was fatigue-critical was topologically optimized and then redesigned for manufacture. A single-piece, multipurpose panel using AM was developed in Bici *et al.* (2018). A discussion of technological limits, aeronautical performances, and sustainability in relation to optimal design and manufacture was presented.

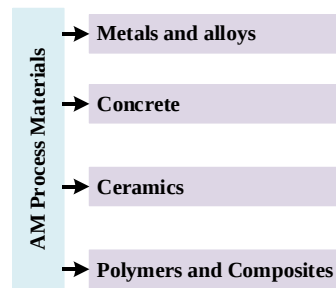


Fig. 7 Materials of AM technology.

Classifications of Materials Used in Various 3D Printing

“How do we create things”, or “how do we transform raw materials into something that we want to buy, use, or consume in any way”, is the very first question that comes to mind when we think of the manufacturing industry. AM, which encompasses a wide range of procedures for producing 3D prototypes and structures from digital information, is one of the manufacturing processes (Blakey-Milner *et al.*, 2021). To create the desired material, several substances are combined in an additive process. There are four materials that can be used in AM illustrated in Fig. 6. All seven different AM techniques shown in Fig. 7 cover the use of these materials, even though polymers are the most often used materials and certain additive methods favor the use of specific components over others (Srivastava *et al.*, 2018). Aspects of the materials used in AM techniques, their viability, their qualities, and their applications are crucial elements in 3DP.

Numerous evaluations that assess and describe the state-of-the-art of metal and alloy processing using AM techniques have been published during the past few years (Murr and Johnson, 2017; Gu *et al.*, 2013). Due to its advantages, such as the creation of complicated geometries, waste minimization, design freedom, and affordable customization, metal AM has recently seen growth. Multi-functional products can be created to address structural, defensive building, and insulating concerns simultaneously (Liu *et al.*, 2021). Using AM with laser metal deposition (LMD), a Cu-9Al-5Fe-5Ni alloy with a hierarchical microstructure and improved mechanical strength was created in Li *et al.* (2021). The development of a modeling and experimental framework that directs optimization of the beam shape dependent laser-metal interaction and the alloy composition was described in Matthews and McKeown (2022) as a science-based method that can solve this weakness and fundamentally revolutionize metal PBF AM. This framework allows for the fabrication of new materials and local part properties. Because of its numerous uses in aircraft, gas turbines, and other structural applications in the high temperature range, Inconel 718 is one of the most commonly utilized alloys in metal additive manufacturing (Srivastava *et al.*, 2021).

By opening up new design possibilities and raising the level of automation, AM processes demonstrate potential and utility in the construction sector (Ekanayaka *et al.*, 2022). To achieve higher component quality, lower test effort, and fewer buildability failures, accurate structural deformation prediction and process parameter optimization are essential considerations. An emerging technology field called AM using concrete has a wide range of possible applications, from furniture and facades to structures (Hanus and Harris, 2013). A significant step toward further automation and application of the technology is the path planning optimization of concrete-based AM. A modular framework for the comprehensive multi-level optimization of path planning for concrete AM was presented in Papacharalampopoulos *et al.* (2020). The primary factors influencing the performance of 3D printed concrete were evaluated in Kristombu Baduge *et al.* (2021), and viable solutions to improve these features were also covered.

In comparison to single-phase ceramic components, AM of ceramic matrix composites (CMCs) has made it possible to produce highly personalized, geometrically complex, and functionalized parts. Additionally, it provides a fresh method for shaping continuous phase reinforced damage-tolerant ceramic composites that are inspired by natural materials (Sun *et al.*, 2023). The use of a sol-gel-based ceramic slurry without the addition of polymeric additives was described in Hur *et al.* (2022) as a revolutionary method for highly dense AM. The most popular fine ceramic substance, alumina, was used as a stand-in for ceramics. A method for extrusion-based AM of a core-shell SiC ceramic composite reinforced by multiple continuous carbon fiber bundles was suggested in Chen *et al.* (2022). A standard nozzle system was adapted to print a water-based SiC paste and continuous carbon fibers at the same time.

Due to its ability to produce complex shapes, more flexible designs, and conductive polymer composites quickly, AM has promise in this area (Yan *et al.*, 2023). The potential of employing composites and polymers in a range of industrial applications, including the architectural, aerospace, medical industries, and toy manufacturing, has been studied for a number of years (Wang *et al.*, 2017). The use of readily available and occasionally underutilized pharmaceutical polymers in AM was encouraged in Govender *et al.* (2021) by systematically elucidating and comparing polymer functional roles and properties for a variety of AM technologies, as well as current and emerging techniques to characterize these properties. The pertinent developments in the AM of conductive polymers and nanocomposites are outlined in Ryan *et al.* (2022), along with a discussion of the benefits and drawbacks of processing and printing these materials in comparison to other conventional manufacturing processes and their inherent properties.

Progress in Materials for 3D Printed Electronics

Utilizing different 3D printing processes in electronics manufacture requires careful evaluation of the materials that can be used and their capacity to scale, from prototyping to full-scale fabrication (Hamidi and Aslani, 2019). Many new materials, including functional materials, nanomaterials smart, materials, biomaterials, and even fast-drying concrete, have been investigated for 3D printing and the use as feed materials for printing actual application parts in recent years due to an increase in demand for both product complexity and multi-functionality (Chua *et al.*, 2018). Smart materials are those that can change an object's geometry and shape in response to environmental factors like heat and moisture (Lee *et al.*, 2017). Self-evolving structures and soft robotic systems are examples of 3D printed items made with intelligent materials. Shape memory polymer's complex shapes might be produced quickly and easily by employing 3DP technology. Based on the dimensional correctness, surface roughness, and part density, the material's quality is assessed (Yang *et al.*, 2015). Food products like meat, chocolate, pizza, candy, sauce, spaghetti, and other ingredients can be processed and produced using 3DP technology to create the appropriate shape and geometry (Kaur *et al.*, 2022). Future moon colonization could benefit from the ability of 3D printing to directly build multi-layered items out of lunar dust (Kalia *et al.*, 2022). With the advancement of 3D textile printing materials, the jewelry and garment industries will flourish (Lee, 2022).

3D printed electronics are constructed using a wide variety of functional materials illustrated in Fig. 8, each with a specific functionality and use (Tan *et al.*, 2022). Active electrical elements made with 3DP are created using semiconductor inks. In (Yuan *et al.*, 2022), new opportunities for the use of inorganic semiconductors in flexible electronics by outlining a plan for producing homogenous semiconductor ink and flexible films on various substrates at low temperatures. Dielectric inks are substances that naturally act as electrical insulators. When it comes to electrode materials for electrochemical sensors and energy storage systems, conductive polymers have significantly increased their market share. The most recent advancements in the targeted alteration of the thin-film microstructure and polymer characteristics predispose them to even more widespread uses in this area (Gmucová, 2022). High quantities of metal-organic complexes or metal salts dissolved in either organic solvents or aqueous solutions make up metal-organic decomposition (MOD) inks (Wünscher *et al.*, 2014). They are also extensively employed in 3D printed electronics applications for the production of electrically conductive traces and patterns. Despite their apparent non-functionality, dielectric materials are crucial for several elements of 3D printed electronics, including capacitor and transistor fabrication, insulation of multilayer circuitry, and circuit protection (Varghese and Sebastian, 2017). The electrically conducting traces in multilayer circuitry are helped to be insulated by the dielectric inks so that conductive inks can be coated on top of one another without short-circuiting while creating multilayer structures. Electrically conducting metallic nanoparticle suspensions in a liquid medium are known as metallic nanoparticle inks. Due to their excellent electrical conductivity, they are frequently utilized for the production of electrically conductive traces and patterns in 3D printed electronics applications (Tan *et al.*, 2019).

The printer's characteristics, the printing parameters, the G-code generating software's capabilities, and the raw material all have a significant impact on the mechanical characteristics and properties of 3D printed objects (Ahmad *et al.*, 2020). Inorganic nanocomposites suspended dielectric inks often offer higher device stability, higher dielectric permittivity, and reduced hysteresis when compared to organic polymeric dielectric inks. Additionally, increasing the filler particle loading or employing filler particles with higher dielectric permittivity can increase the dielectric permittivity in inorganic nanocomposites suspensions dielectric inks (Li *et al.*, 2018). The particle shape of metallic nanoparticles may have an impact on their electrical, optical, magnetic, and catalytic

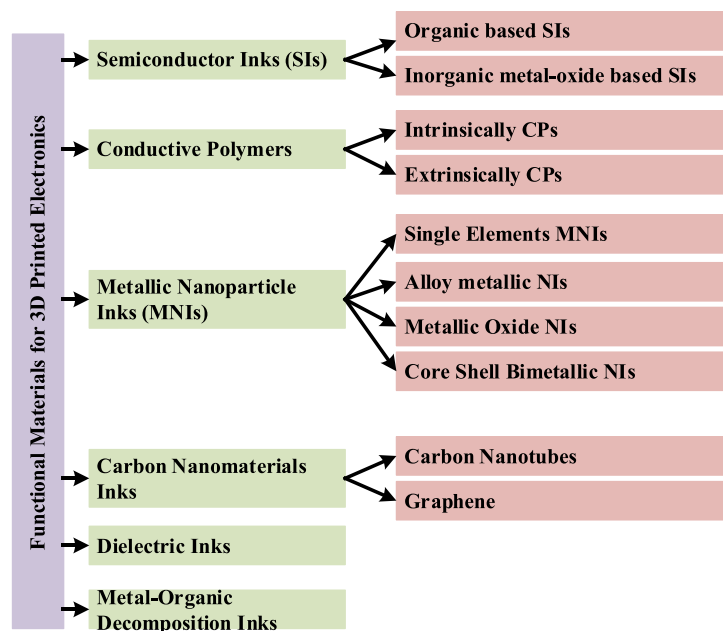


Fig. 8 Progress in functional materials for 3D printed electronics. Adapted from Tan, H.W., Choong, Y.Y.C., Kuo, C.N., Low, H.Y., Chua, C.K., 2022. 3D printed electronics: Processes, materials and future trends. Prog. Mater. Sci. 127, 100945. Available at: <https://doi.org/10.1016/j.PMATSCI.2022.100945>.

capabilities (Rajan *et al.*, 2016). Some of the few intriguing particle morphologies that have recently attracted increasing notice include nanoplatelets and nanowires.

Current Challenges and Future Outlook

Both potential and difficulties exist for 3DP electronics. The sector has the ability to change as a result of new material developments, digital designs, printing methods, and printing protocols. This most recent technology has the potential to be revolutionary, and applications for 3D embedded electrical devices, 3D conformal electronics, flexible 3D printed electronics, and stretchable 3D printed electronics are expected to dominate future research (Tan *et al.*, 2022).

Each of the process or technique may have material limitations, build volume and resolution restrictions (shape accuracy limitations), and system integration restrictions. Although design and customization options are flexible, there are still significant build quality and spatial resolution challenges to be solved (Espera *et al.*, 2019). Despite having several benefits, it is difficult to forecast or fully understand how processing settings affect the characteristics of metal AM products. High accuracy-based machine learning (ML) models are required for predicting and understanding the shape and different sorts of faults in metal AM (Lee *et al.*, 2023). The high polymeric concentration of the ceramic feedstock materials has made AM of thick ceramic items difficult. However, the binder and additives have remained in the polymeric composition despite numerous studies to enhance the ceramic percentage in the feedstock (Hur *et al.*, 2022). The conventional approaches to the preparation of SiC ceramic composites reinforced with carbon fiber have significant drawbacks due to their high cost, labor-intensive preparation procedure, and challenging structural design (Chen *et al.*, 2022).

Currently, the majority of affordable 3D printers have poor resolutions that make it difficult to create micro-scale structures and cause surface roughness from material deposition on the surface or uncured particles. The print resolution now offered by cost-effective printers is, at best, a few orders of magnitude below what is necessary to produce workable stationary beds for high-performance separations that really take place, or even large capacity SPE phases. However, the technology is advancing at a remarkable rate, and ongoing advancements in the resolution of commercial 3D printers, along with an expanding selection of printing materials, will enable in the very near future to surpass the current constraints (Kalsoom *et al.*, 2018).

By providing a speedy and affordable alternative to more conventional manufacturing techniques like shaping, molding, and computer control machining, 3DP, continues to have an impact on manufacturing and prototyping (Low *et al.*, 2017; Rayna and Striukova, 2014). There are a number of challenges to the use and development of 3DP in the manufacturing sector (Pirjan and Petrosanu, 2013). For instance, the use of 3DP technology would diminish the need for manufacturing labor, which will immediately have a significant impact on the economies of nations that rely heavily on low-skill occupations. Additionally, users of 3D printing technology can manufacture a wide variety of objects, including firearms, knives, and other hazardous goods. As a result, the usage of 3D printing should be restricted to a small group of people in order to stop terrorists and criminals from bringing guns into the country undetected. In addition, anyone with access to a blueprint will be able to produce fake goods with ease (Shahrubudin *et al.*, 2019). While AM is still in its infancy, gathering data regarding the requirement to produce defect-free, high-quality goods at a low cost in a hurry still remains a crucial objective. Over the course of several millennia, more study and advancement in AM techniques will be needed to meet this goal (Ryan *et al.*, 2022).

Conclusions

Currently, 3D printing is evolving to be potential technology in the production sectors due to its advantages for individuals, businesses, and the government. The popularity of this quick and flexible fabrication technology is rising as a result of the recent trend toward fully automated miniaturized instruments. The potential for producing stationary phases and columns on a print-to-order basis, along with the ongoing development of new printing materials, could hasten the creation of highly customized, delicate, and selective platforms. Additionally, the advent of multi-material printers offers the possibility of producing a variety of components utilizing materials with different properties, including columns, stationary phases, flow connections, etc. Therefore, more involvement and research are required to accelerate the adoption and development of 3D printing with the aid of additional information. The sustainability of 3D printing and its ability to lessen CO₂ emissions and total energy utilization because of industrial fabrication are crucial factors in the advancement of re generation schemes. This study finds that significant efforts are being made to increase scientific knowledge of additive manufacturing techniques, component properties, and structures.

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Conflicts of Interest

The authors declare no conflict of interest.

Author Contributions

All authors have equal contribution to prepare and finalize the manuscript.

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Nanobots: Self-Regulated Electronics for Health Care

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Abstract

Nanobots are very small, self-regulated and propelled electronic devices or bots that are either pre-programmed or can be controlled from outside to do specific work such as detection, operation or diagnosis. The devices range between 0.1 and 10 micrometers and are constructed with nano scale molecules or molecular compounds. The main distinctive advantages of nanobots over other conventional or novel dosage form are complete control over the bots at any given time and very less chance of any adverse effect. This article introduces types and structure of nanobots followed by a comprehensive compilation of different applications of nanobots in medical treatment.

Key Points

- *Nanobot* is a self-propelled device having a dimension in the nanometer range which interacts with the human body in the cellular level for targeted delivery of drug or any other precise medical treatment.

Introduction

Nanotechnology has become the fastest-growing field in engineering, particularly in electronics, agriculture, biomedical, cosmetics, food, pharmaceuticals, and construction industries. Nanotechnology is often termed as the industrial revolution of the twenty-first century, which is continuously changing the science, education, manufacturing, communication system and the lifestyles of people around the world ([Khan and Asmatulu, 2013](#)). The concept which was still a subject of science fiction movie in 1966 on the film 'Fantastic Voyage' where a submarine crew shrunk into microscopic size and entered into a scientist's body to repair his damaged brain ([Menville and Reginald, 1977](#); [Fu and Yan, 2012](#)) has now become a semi-reality. Nowadays, it is actually possible to create such micro or nano-sized particles programmed to treat ailments and disorders. This has been achieved through the help of nanotechnology.

Nanotechnology served as a boon and presented the mankind with its extraordinary invention of a device called 'nanobot'. The word 'nanobot' simply depicts very small (nano) robot (bot). The term nanobot came into use during the late 1990s and early 2000s. Prior to 1998, nanobots was mentioned as 'molecular machine' or 'nanomachine' or 'cell repair machine'. Eric K. Drexler and Robert A. Freitas are the two pioneers who made the nanobot term popular ([Mavroidis and Ferreira, 2013](#); [Nistor and Rusu, 2019](#)).

Nanobots are characteristically controllable machines fabricated with nanometric components ~50–100 nm wide ([Rifat *et al.*, 2019](#)) that can interact and even perforate the cellular membrane, providing a direct pathway to the cellular level. Nanobots have the capability to achieve several single or combinatorial functions including actuation, impulsion, sensing, signaling and information processing. These nanodevices can be applied very efficiently for drug delivery ([Nistor and Rusu, 2019](#); [Subramani and Mehta, 2018](#); [Singh *et al.*, 2019](#); [Zeeshan *et al.*, 2011](#)). The nanobots are also called by different terms such as nanorobots, nanites, nanoagents and nanoids ([Mavroidis and Ferreira, 2013](#); [Rifat *et al.*, 2019](#)). These nanodevices have been recently used in biological system control such as aiming the drugs to a particular site of action i.e. target specific delivery which would make the drug much more effective and decrease the chances of possible side effects. The main significance of control design of these nanobots is molecular manipulation to accurately diagnose and treat the disease on a cellular level accuracy. Besides, nanobots have a great advantage for controlling the amount and time of drug release through monitoring the electrical pulse ([Nistor and Rusu, 2019](#); [Subramani and Mehta, 2018](#)). Nanobots have been found useful as bio-nanomachines of the future for the development of effective medical treatments due to their long durability, faster functionality and capability of targeted drug delivery directly to the specific diseased cells. Nevertheless, further research is to overcome the current problems such as high costs related with preliminary development, tremendously complicated design, susceptibility to electrical interference for, e.g., radio frequency or electric fields and electromagnetic pulses produced by external sources ([Nistor and Rusu, 2019](#); [Subramani and Mehta, 2018](#); [Singh *et al.*, 2019](#)).

The most renowned potential application sector of nanobots is to diagnose, analyze and treat cancer without noticeable adverse effect ([Tripathi and Kumar, 2018](#)). Viral infections which lead to the formation of cancer, i.e. the human papilloma virus (HPV), may be suppressed by using nanobots for targeted drug delivery system for cancer treatment. In this domain a new aspiration is to create biological nanobots using the strands of DNA to create non harmful nanobots. Nanobots can also be used for the innovative treatment of many other diseases such as AIDS, diabetes, cystic fibrosis, neurodegenerative disease, heart diseases, oral disease as well as the construction new solutions in gene therapy, surgery, nanoneedles, damaged tissue repairing, etc. Though currently no

nanodevice or nanomachines are undergoing clinical trials, some of them showed promising result at animal trials (rat, mice) (Nistor and Rusu, 2019). The current article describes about nanobots and their applications in various drug delivery systems.

Design and Types of Nanobots

According to the structure and configuration nanobots can be categorized into two major classes - the organic nanobots and the inorganic nanobots.

Organic nanobots are also known as bio-nanorobots. They are manufactured using DNA of virus and bacteria or proteins (Bhat, 2014). These types of nanobots cause least amount of toxicity and adverse effect and are the most body friendly among all. The inorganic nanorobots are prepared with artificially produced diamond shaped protein and other types of materials (da Silva Luz *et al.*, 2016).

Inorganic types of nanobots are composed of carbon in the form of diamond or fullerene nanocomposites because of their high strength, inert properties and high performance. These nanobots may cause inflammation and cell toxicity upon application due to the incidence of rejection reactions from the host immune system. A way to counter to overcome these problems is to cover the outside surface of the nanobots with a passive diamond layer or with biodegradable materials such as lipids and proteins (Nistor and Rusu, 2019). The main advantage of inorganic nanobots over organic one is they are more controllable and accurate yielding high chances of programmed response and accurate dosing (Wang, 2009).

Apart from the traditional classes described above, recently there have been some new developments in the field. A team of scientists from South Korea developed a special type of nanobots known as bacteriobots. A bacteriobot is created when a modified salmonella bacteria is combined with the chemical components for targeting cancer cells. The salmonella bacteria DNA is modified in such a way so that it causes minimum toxicity or no toxicity at all. When the bacteriobots reach the destined cancer cells they release the cytotoxins affecting only the cancer cells. The bacteriobots are designed to attack the colorectal tumor cells and the test showed a positive result when tried on laboratory mouse (Han *et al.*, 2016). Besides bacteriobots, some recent literature also described two other types of nanobots: magnetically driven nanorobotic systems and large nanomanipulators with nanoscale manipulation ability (Nistor and Rusu, 2019).

A nanobot may consist of different basic elements depending on the application. The components can be vastly heterogeneous in nature, such as a power source, sensors, actuators, onboard computers, pumps, and structural support. Besides the basic elements, particularly for biomedical purposes, the nanobots may contain several substructures depending on the requirement of the treatment, e.g., a payload compartment for holding the medication dose, a miniature video camera for manually navigating through the body, lasers for removing harmful materials, or microwave emitters and ultrasonic signal generators for killing cancer cells. The chemotactic sensors can be used to detect and distinguish between different cell types through a process that includes identification of their surface antigens. Finally, a propulsion tail is essential for the active movement of nanobots (Nistor and Rusu, 2019).

Nanobots are going to emerge as one of the futuristic drug delivery system providing targeted delivery with cellular level accuracy. There are two major reasons behind the speculations, first, doses and frequency can be accurately adjusted before administration, and second, targeted delivery of drugs for articular and ventricular disorder, cancer, dental problem, diabetics can be achieved (Hamdi *et al.*, 2008).

Nanobots for Drug Delivery System

According to the design, construction, and more importantly, their uses as drug delivery system, nanobots can be classified as (Kumar *et al.*, 2014):

Pharmacytes

Pharmacytes are special type of medical nanobots having a size up to 1–2 μm and they can carry up to 1–3 μm of drug to a specific site via drug tanks. Upon reaching the predestined cellular site they release the drug with the help of nano-injection via progressive cytopenetration process until the payload of drug delivered completely (Robert, 2005).

Respirocytes

Respirocytes are tiny nanobots design to perform the work of red blood cells. It is tightly packed and arranged mass of molecule ranging up to 1 μm and can carry oxygen and carbon dioxide in systemic circulation (Mishra *et al.*, 2012). It has been reported that one unit of these respirocytes can carry 236 times more oxygen compared to normal red blood cells and 5 trillion of these units can function as oxygen supplier for whole 5.4 liters of blood (Arpita *et al.*, 2013).

Microbivores

Microbivores completely devour the harmful pathogenic microbes and other microorganism. It functions like a white blood cells and are referred to as nanorobotic phagocytes (Freitas Jr., 2005c). Generally spherical, these devices are prepared by highly

compressed diamonds and sapphire. These micromachines have a diameter of approximately 3.4 μm containing 610 billion precisely organized molecules. They entrap the pathogen present in blood and break it down to molecular level (Freitas Jr., 2001).

Clotocytes

The process of blood clot formation is known as hemostasis. Generally, the process of blood clotting is accomplished within 2–5 min upon receiving the wound (Freitas Jr., 2000a). This process starts when the platelets rush towards the damaged collagen of blood vessel and starts forming net like aperture with help of other clotting factors. Clotocytes have been successful in drastically reducing the clotting time (Freitas Jr., 2000a). Clotocytes are artificial mechanical programmed platelets which are almost 1000 times faster to perform hemostasis than body's normal hemostatic system. Powered by serum-oxyglucose and containing biodegradable fiber mesh, these clotocytes could cure diseases like hemophilia (Schneider *et al.*, 2006).

DNA Nanobots

DNA nanobots are example of extreme targeting drug delivery system. They are specific up to the cellular level. As the name suggest they are entirely made up with DNA, programmed to configure as an origami like structure (Behkam and Sitti, 2006). DNA nanobots can alter its molecular configuration and can be used in sensing, computing or as a therapeutic nanodevice. For example, the rectangular sheet of nanodevice configured as an origami structure is programmed with a specific type of blood clotting enzyme and thrombin. DNA fastener is used to fasten the edges of long end of DNA. This results in a cylindrical structure of DNA containing thrombin in the center of the structure (Cavalcanti *et al.*, 2008). The fasteners are predesigned to dissociate when they come to contact with a protein specific only to the surface of tumor blood vessels cells. At this point the DNA structure unfolds and exposes the inner components to that specific cell (Nandkishor *et al.*, 2014). These nanobots place themselves on a specific portion of blood vessels which carries nutrients towards the malignant tumor cells. Within 48 h they cause excessive clotting of blood in that particular blood vessel, causing almost complete blockage of that particular blood vessel resulting in shortage of oxygen or nutrients or both. As a result, the cancer cell dies slowly with time asphyxiation and malnutrition. The most noted feature of this technique is the clot only appears on that targeted particular blood vessels and not in any other or neighboring blood capillary. Further evaluation test showed that there is no toxicity residue remains after the operation is done so chances of cytotoxicity are very less and also no significant inflammation is found (Hussan *et al.*, 2011). The safety preclinical trial was done with Swiss albino mouse. The mouse was injected with human breast cancer cells, then the DNA nanobots were introduced to system in intravenous route and within 48 h significant result was found. Lastly, the safety concern of nanorobots was tested in Bama miniature pigs, whose anatomy and physiology closely resembles with human (Debjit *et al.*, 2009).

Application of Nanobots in Medical Treatment

Nanobots are potential advance drug delivery system for most accurate and targeted specific drug delivery with low adverse effect compared to other delivery system (Barbosa *et al.*, 2015). We have covered the most common types of nanorobots for drug delivery in the previous section, but depending on the medical treatment, there are a plethora of design and construction varieties as described in the following subsections.

Surgery

Surgery is a specified branch of medicine that employs operating the specific site for treating any disease or injury. It also involves physical alteration of tissue or organ. Surgery is expensive and a time-consuming process, but the limitations of surgery can be overcome by using nanobots (Mali, 2013).

The nanobots are the miniaturized robots which enter the body across the cavities and are controlled by the surgeons using a computer (Freitas Jr., 2005b,d; Cavalcanti *et al.*, 2008; Deepa *et al.*, 2010). Inside the body, surgically programmed nanobot can act as a semi-autonomous onsite surgeon, to ensure optimum, safer and accurate treatment. It also can perform different types functions such as diagnosis or correcting lesions by nanomanipulation coordinated by an on-board computer (Freitas Jr., 2005a). The main advantages of nanorobot-based surgery are, it is safer, surgeon always have full control over the mercenary at any given movement, and it is highly patient convenient as it does not require painful big cuts to operate. Nanobots enable the surgeons to go for minimum invasive methods to cure the patients and their recovery is also faster due to less scarring.

Some of the novel avenues for nanobots in the surgical domain are as follows:

Nanocoated surgical blades

These are the new surgical tools which are manufactured in nanometer range which are similar to a surgeon blade. These can be used more effectively on patients with reduced trauma by less incisions. These can be upgraded by using micro structured hard metal coating with diamond and processing. These blades will have the cutting range in the diameter region of 5 nm – 1 μm . These blades have been used in the eyes, treatment of neurosurgery and minimum invasive surgery (Bogedal *et al.*, 2011; Roszek *et al.*, 2011; Lingenfelder *et al.*, 2005).

Nanoneedles

These are composed of silicon which used in combination of an atomic force microscope to invade the nucleus of cell and deliver the drug molecules. They are also used in surgical procedure. The nanoneedles are 6–8 μm in length and 200–300 nm in diameter (Bogedal *et al.*, 2011; Observatory, 2009; Roszek *et al.*, 2011). In atomic force microscopy using a nanoneedle a probe is used to scan throughout the sample for obtaining information about the surface and also identifying unique properties by contact of the cell using ultrathin nanoneedle. By this technique we can induce differentiation from the stem cells to manufacture better healthy cells and donate to the patient. Besides the scanning mode, atomic force microscopy can also perform tapping mode to determine the elasticity of a single cell, and/or attach a molecule to study protein-protein interaction.

Catheters for minimally invasive strategy

Catheters are inserted into the body for injecting or draining fluids or keeping the passage clear but the main problem is thrombus formation above the device surface. To overcome these nanomaterials such as nano tubes have been put into catheters by minimum surgery to increase their strength as well as reduce the thrombogenic effect (Bogedal *et al.*, 2011; Observatory, 2009; Roszek *et al.*, 2011).

Wound dressing

Advanced wound dressing is possible with nano-silver-bots. Metallic silver has anti-infective properties. It can be used against various bacteria and microorganisms. Scientists have developed a nano porous silver powder. The smaller particles have great surface area and therefore a better anti-infective agent. Silver is required in very less quantity so chances of toxicity are less. The nano silver enters the body fluid through wound and takes 30 min to kill the bacteria. These dressings are durable and its durability depends on the thickness of the nano silver (Roszek *et al.*, 2011; Freitas Jr., 2005a; Smalley, 2001).

Damage tissue repairing

Nanobots can easily repair or heal damaged tissue by reconstructing the essential elements and replicate the tissue while disposing the damaged cells and tissue. Replacing the damaged tissue and reassembling the new tissue is the general concept to be applied to perform healing operation by nanobots. It works by slowly reassembling the tissues, layer by layer, and ultimately reconstructing the whole tissue. It also can regrow the damaged bones slowly (Freitas Jr., 2002). Scientists are trying to replicate the bone marrow with the help of nanobots. Other possibilities include closing of split vein, reforming of damaged skin, removing dead tissue and flesh etc. Once successfully applied, it can cure some special medical condition, complex fracture and permanent marks on skin (Thorek *et al.*, 2006).

Oral Treatment

Nanobots which are designed to apply in oral and dental treatments are commonly known as dentifrobots. These tiny dentifrobots are used generally in conditions like tooth whitening, routine cleaning of tooth, hypersensitivity and even for orthodontics purpose. It also can accurately detect oral cancer and can be used in treating that. These nanorobotic dentifrices generally applied with the help of tooth paste or mouthwash, as a result the whole subgingival surface can be covered by them very easily. Main functions of these tiny bots are to metabolize the micro residue left in teeth junction. They also can exterminate the harmful and pathogenic organism if properly programmed (Nandkishor *et al.*, 2014). These harmful organisms generally grow inside the dental plaque and dentifrobots can eliminate them by attacking them omnidirectionally. Dentifrobots after performing its destined task deactivate themselves and become completely harmless, excretion of these bots done by urine (Shetty *et al.*, 2013).

The various purposes that dentifrobots can serve are (Amir *et al.*, 2014):

Diagnosing/treating oral cancer

Identification of severity of the cancer in oral region can be accurately identified by dentifrobots. In this process the saliva is used as genomic and proteomic bio marker that helps in molecular disease identification. Primarily, nanosensor test of oral fluid and optical biosensor are being used to diagnose the oral cancer. Oral cancer treatment is generally done with the help of nanoshells, which selectively eradicate the cancer cells without damaging the surrounding normal cells (Li *et al.*, 2018).

Nanoanesthesia

The nanobots can be used to induce anesthesia in dental region. Millions of tiny dentifrobots are loaded with anesthetic agents which is then incorporated in gingiva. After incorporation they travel through gingiva sulcus to reach pulp. These tiny nanobots are incorporated through colloidal suspensions containing millions of tiny nanobots (Jain, 2005). Anesthetics given by nanobots are fast, reversible and patient compliance is very high as it restores the sensation of the dental region after operation is done and gets excreted via urine and stool without damaging the surrounding tissues or creating any adverse effect.

Suppressing hypersensitivity

Hypersensitivity is mainly caused by thermal stimulation and hydro dynamic pressure alteration in the pulp. Hypersensitive teeth have almost 2 times higher tubule diameter and 8 times higher sensitivity compared to normal teeth. After incorporation of

nanobots in these region nanobots can easily obstruct the tubule zone in a matter of minutes by using locally available building materials, closing of the excess diameter of tubule, and providing relief to patient quickly and permanently (Goldberg *et al.*, 2003).

Orthodontics

Orthodontics nanobots can perform tooth up righting, vertical repositioning and rapid tissue repairing. Nanotechnology embodied stainless steel wire is being studied as potential orthodontics material. It is the combination of ultra-high strength with ability of deformation, corrosion resistance and inert in nature (Poonia *et al.*, 2017).

Tooth repairing

The whole tooth is replaced including both cellular and mineral components. This process is known as complete dentition replacement (Freitas Jr., 2000b).

Treatment of Liver Cancer

In the liver, several types of cancer can form, the most common being hepatocellular carcinoma, while other types of liver cancers include hepatoblastoma and intrahepatic cholangiocarcinoma (Behkam and Sitti, 2006). For a primary or metastatic liver cancer patient, surgery is a central part of the treatment. Surgery is also a crucial part even in combination treatment, where surgery is combined with systemic chemotherapy for treating metastatic colorectal cancer to the liver.

Nanorobots are small in size, easily disposable and can realize automated painless treatment. It is an inexpensive (if mass produced) process and no maintenance is needed. Nanobots have advantages like surgical precision, leading to less blood loss and improved outcomes overall. It allows the doctor to live time monitor the condition of liver and surgeon has total control over the situation at any moments (Raj and Ranjith, 2017). Liver is present in the right upper quadrant of the abdomen, and open surgery requires a very large abdominal incision both under the ribs and extending to the midline (Narayanan *et al.*, 2006). With nanorobots, liver tumors can be treated with minimally invasive surgical approaches, which can avoid needs of large incision and facilitate effective removal of tumor. The liver is divided into two lobes and is also subdivided into eight segments. In the liver surgery the main goal is to remove the tumor while maintaining liver functions like blood flow in and out of the liver. Different types of nanorobots are applicable for the treatment depending on the location of the tumor and the biology of the disease process. For liver periphery tumor either a segmentectomy or wedge resection is often adequate (Xie *et al.*, 2007). The segmentectomy is surgical removal of one of the liver's eight segments and wedge resection is the process of removal of the tumor along with some surrounding liver tissue. In case of larger and more centrally located tumors, the formal right or left hepatic lobectomy is more appropriate which removes one of the liver's two lobes.

Treatment of Diabetes

The normal blood sugar level is approximately about 130 mg/dl. Variation of ± 30 mg/dl can be considered as range of displacement, though it can be altered depending upon the particular medical condition. Nanobots can be reconstructed in such a way that it can monitor the slightest difference between standard reading and altered reading (Deepa *et al.*, 2010). If the practical readings vastly differ from theoretical value and reaches critical level then it can alert the patient by sending radio wave as warning message to the smartphone, it also can warn the doctor about the condition of the patient.

Also, unlike regular medicines which just suppress the cause of diabetes, nanorobots have the potential to actually cure the disease to its root (Patel *et al.*, 2006). This is possible with human sodium glucose transporter type 3, which has significant role in controlling the extracellular glucose concentration, thus controlling the concentration of glucose present in blood. This enzyme works as the regulator.

Treatment of Neurodegenerative Disorder

Neurodegenerative disorders affect the life's quality (Schrag *et al.*, 2000; Hebert *et al.*, 2003). Neurodegenerative disorders like Parkinson's, Alzheimer's disease, schizophrenia or paraplegia are expected to be treated as the nanobot technology advances. The method of inserting nanobots into the neural circuit has been derived from the principle of 'endomycorrhiza' (Brundrett, 2002). Endomycorrhiza is a type of fungus which develops a symbiotic relation with plants by attaching themselves to the plant roots and deriving nutrition from them, in turn protecting the plant from invasion of pathogens and promoting their growth (Tahat *et al.*, 2010).

An idea of designing nanobots in a way has been thought which can fix the glitch in the neuronal network of the persons suffering from any kind of neurodegenerative disorders. This design is being called as the endomycorrhiza like interface (ELI). This ELI will consist of a central chamber surrounded by a mesh made of nanobot. The central chamber will be consisting cations. The central chamber will be connected to several neurons by the nanobot mesh. In response to an action potential from any of the connected neurons, cations will be released from the chamber. The mesh has some fibers that are radially extended from the mesh to attach with neuronal body, the axon or the dendrons (Saniotis *et al.*, 2018).

This ELI should be made target specific by inculcating within them the characteristics of ligands to facilitate its binding to only specific receptor site (like axon membrane receptor). Delivery of the nanobot into the brain bypassing blood brain barrier will be achieved by directly injecting it into the cerebrospinal fluid moving through the fluid with the help of a propeller designed in it up

to its desired site (Veisich *et al.*, 2015). As far as the immune response is concerned, the scientist has thought of tricking the immune system so that they do not attack the ELI (foreign body) by certain methods (Xie *et al.*, 2007).

Till now the entire thing is but a mere hypothesis which we can hope to soon be useful to the mankind. The viability of development of this nanobot containing ELI can only be answered by the research that's currently going on hippocampal prosthetics for replacing memory and recovering patients with Alzheimer's disease (AD) and cerebral trauma (Berger *et al.*, 2012). The positive thing is that the advancement in medical science dealing with neurological aspects is giving us hope for the possibility to develop or design a model as mentioned above.

Treatment of HIV

HIV is a special type of retrovirus that targets the human immunity system. HIV leads to a medical condition known as AIDS, which demonstrates complete breakdown of immunity system resulting in multiple diseases with no immune retaliation, by slowly exterminating the white blood cells (Mamo *et al.*, 2010). White blood cells which are responsible to fight against diseases get completely destroyed in this medical condition. Unfortunately, there are no drugs currently present which can completely cure AIDS. Using nanobots, AIDS affected WBCs can be converted back to their original form and thus body is able to maintain its immune system (Date and Destache, 2013).

Treatment of Genetic Diseases

Nanorobots have the ability to treat genetic diseases. A special nanobot can be designed which can compare the molecular structures of DNA and proteins in the cell to the desired reference structures. After that any kind of irregularities can then be corrected and modifications can be done. Inside human cell in the nucleus there is an assembler built repair vessel which is responsible for genetic maintenance. The nanorobot performs stretching of supercoil of DNA by its lower arms and pulls the unwound strand by an opening for analysis. Then the molecular structures of both the DNA and proteins are compared to nanocomputer database. The irregularities can then be corrected (Regan *et al.*, 2011).

Conclusion

Nanobots are one of the developing therapies in today's world, having a promising future in the pharmaceutical field. Already a lot of experimentations and researches are going on to use them for therapeutic purposes. They opened new probabilities in the treatment of diseases such as cancer, neurodegenerative disorders, repairing tissues at molecular level, drug targeting etc. In the future nanobots will play an important role in the pharmaceutical industry for optimizing target specific drug delivery to a certain location with a precise release mechanism and also could be programmed to repair specific diseased cells, working in a similar pathway of our natural healing processes. Although nanobots have several advantages for implantation in drug delivery system, they have limitations for successful clinical applications. Thus, more research is required to fabricate large batches production with low cost and accurate control over shape/size in structures and components.

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Development of Conductive Polymers as Potential Sensor Material for Wearable Electronics

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Abstract

Miniaturization of modern electronic devices, development of fabric and sensor materials and the integration of miniature device/sensor with the fabric helps the emergence of smart wearable technologies. The wearable systems are becoming more popular due to the rapid development of modern electronic materials and the manufacturers are trying to meet new requirements of the electronic devices including low weight, small size, flexibility, extreme production power, nonstop great production ability, relaxed integration with or within the clothing fabrication procedures. However, challenges are still remained to solve such as the washability features that needs to be merged into e-textiles to carry market gains in various applications, including sports and healthcare where the people can easily wear as normal daily clothes. Conventional electronic materials are not fully capable of efficiently meeting the washability requirement due to their rigidity and bulkiness. Still, several technical and non-technical issues of the materials are required to be addressed. Conducting polymer is one of the important electronic materials which is continuously being developed driven by the emerging innovations in sensor and textile materials, nanotechnology, etc to overcome the challenge. This article presents the fundamental background of the conducting polymers, and presents their technological development with some recent applications. Challenges and future development opportunities are also critically discussed.

Introduction

It is crucial to improve materials and resources for the advancement of human life due to the rapid progress in technology. Designing and developing sensor and biosensor, large number of nanostructured materials along with conducting polymers (CPs) have become extremely prevalent (Sołoducho and Cabaj, 2016) due to their favorable properties. Nowadays, smart sensors based on flexible materials have opened up huge possibilities for research by cutting down the structural hurdles of the conventional sensors (Zahid *et al.*, 2022). Due to having rigid mechanical characteristics, differed from the textile-woven structures, the conventional sensors and related appliances are not fully compatible. Therefore, flexible polymeric materials showed potentials to develop smart material. Global research and development have typically presented further involvement in developing sensors as evidenced through published literature, financial contribution, and research since the last 20 years (Zahid *et al.*, 2022). Various sensing gadgets and wearable sensor devices have been developed for environmental and medical applications through the recent research efforts (Sempionatto *et al.*, 2019). The basic component among the wearable devices are conductive polymers, which can enhance smart monitoring through their optical and electrical properties. For example, actuators and sensors are implanted within the textile which are electrically powered and operated by electronic devices (Takei *et al.*, 2019). The CPs can be synthesized by electrochemical and chemical processes and they are sensitive to analytes at ambient condition (Sołoducho and Cabaj, 2016). Furthermore, the CPs have fundamental transport properties including electrical conductivity, energy transferring rate etc. Modification of polymer structure can also be performed to provide response toward a specific analyte. Furthermore, sensitivity can be tuned by adjusting the artificial variables for example combined counter ions or polymerization temperature. Sensor array can be developed using electrochemical deposition, which enables miniaturization and bulk manufacturing of the sensor device.

CPs have been persisted in the field of polymer science since the last decades (Idumah, 2021). CPs intrinsically crossbreed the mechanical behavior of natural polymeric objects with charge flexibility and having opto-electronical behavior which are simpler to adjust in association with metals and semiconductors. The expansion in the scope of CP's multifunctional applications happened due to their structural control and nanocomposites design. These advantageous performances have taken the benefit of development in actuators, sensors, energy converting and storing systems, biomedical and other entities. Fundamentally, the CPs are a remarkable group of organic objects that can be synthesized easily with a wide-ranging chemical architectures and versatile range of micro- and nano-architectures to realize a tailored organic, macroscopic and physical behaviors. Fig. 1 shows some common conducting polymers which are being used for developing advanced materials.

Tension, pressure, vibration, force, etc., are known as mechanical stimuli which are transduced into electrical constraints by wearable sensors. In such case, piezoresistivity, capacitance and piezoelectricity are commonly used as the conventional mechanisms of the wearable sensors (Lund *et al.*, 2018). Strain devices based on piezoresistive are developed with electrically conductive sensing films, which are attached with flexible substrates. Temperature, pH, humidity, etc., are measured by the sensors (Lee *et al.*, 2016; Wang *et al.*, 2017). Capacitive wearable sensors have superior flexibility, sensitivity, strength and steadiness. These sensors are developed with quadripartite textile electrode and air-fluorosilicone dielectric for detecting physical parameters of human bodies. Flexible strain or pressure sensors are developed by either coating or embedding those into the flexible polymers with the use of inorganic piezoelectric materials, including ZnO, GaN and PZT (Liu *et al.*, 2018). However, CPs demonstrate exclusive properties for having existence of various elements, blended effect and found applications in numerous fields (Zahid *et al.*, 2022) as presented in Fig. 2.

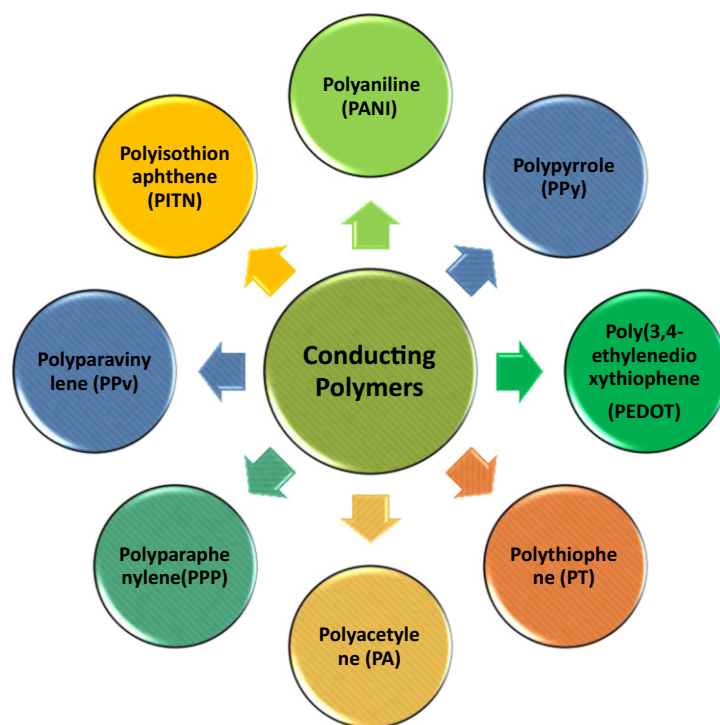


Fig. 1 List of current common conducting polymers.

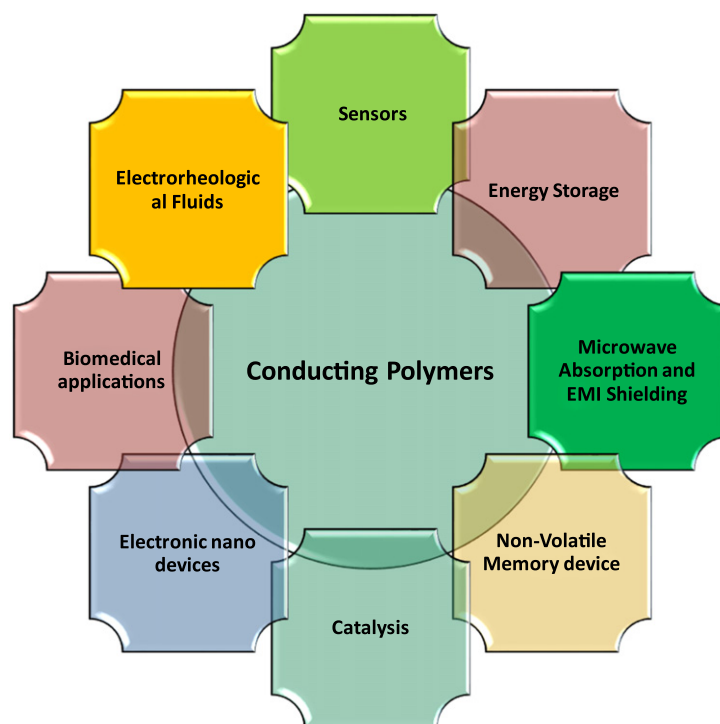


Fig. 2 Current applications of conducting polymers.

Numerous integration techniques are applied namely, compounding, coating, printing and drawing by using the conducting materials for example in smart clothing. During compounding, dried elastic composites are made as film forms to meet the application requirements of the smart clothing. To accomplish this, active sensor materials are doped into polymers (Shimojo *et al.*, 2004). To produce electrically conductive textiles, coatings are employed to the surface of fibers, yarns, or fabrics (Liu *et al.*, 2018). However, there are many

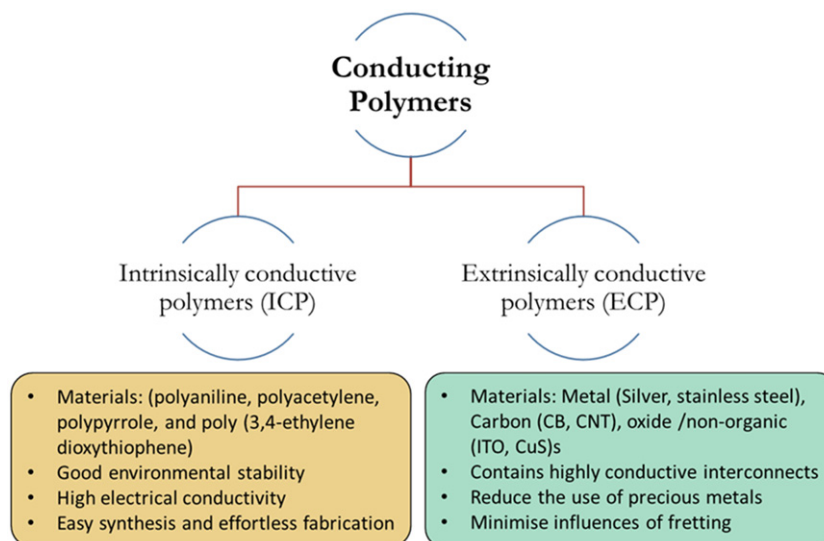


Fig. 3 Basics of Conducting polymers.

pattern transferring techniques are found including screen-printing, inkjet printing, 3D printing, handwriting, micro-scale modeling and lithography. Micro-scale modeling can help in preparing microstructure in substrates, electrodes, and sensing composites. 3D printing is used for developing functional constructions and building flexible/stretchable sensors (Meyer *et al.*, 2010). Lithography, another technique, has the capability in fabricating complicated stretchable systems with correct dimension, gentle composition and strong functionality. Carbon particles are blended for developing a coated material. In addition, conductive yarns are formed using staple metal fibers, filaments of metals etc. For developing smart clothes, the coating technology would be ideal as the coatings is applicable to the surface of fibers, yarns, fabrics, etc., to produce electrically conductive cloths or textiles.

Conducting Polymers

It is known from the state-of-the-art literature that several disciplines have contributed to research in this area and enhanced the CPs, which can conduct electricity in a broad range and retain their polymeric mechanical properties (Fomo *et al.*, 2019). It demonstrates a conductive or a semiconductive behavior. Diverse polymers are developed including polyacetylene, polyurethane, polyaniline, etc., for developing the smart devices. These polymers demonstrate electrical and mechanical attributes and have shown comparatively high regulating electrical conductivity with having characteristics such as biocompatibility, lightweight, flexibility, and comparatively cheaper. CMs blended the important characteristics of traditional polymers and alloys (Rashid *et al.*, 2020). CPs are separated into two categories including intrinsically conductive polymers (ICP) and extrinsically conductive polymers (ECP) which has been summarized in Fig. 3.

Intrinsically conductive polymers have lengthy conjugated dual bonds in their backbone chain which merges to create intrinsically conductive polymers. The existence of the dual bonds represents the sign of improved conductivity of polymers where chemical oxidative and electrochemical methods are used for synthesis. Poly (3,4-ethylene dioxythiophene), polyaniline, polyacetylene, polypyrrole, and a derivative of polythiophene are the main materials for the CPs. These materials have decent eco-friendly solidity and extreme electrical conductivity. To enhance low solubility of Intrinsically conductive polymers (ICP), improvement in solution processing is conducted. A polymer maintains double requirements to make it conductive where the condition number one is the involvement of conjugated double bonds and the other condition is that the polymer configuration is required to be intermittent by adding or removing electrons from it.

Extrinsically conductive polymers (ECP) are synthesized either by conducting melt combining or solvent blending of thermosetting plastic, thermoplastic or insulating polymer materials with conductive protective material (Zahid *et al.*, 2022). Filler contains various materials including Silver, stainless steel, carbon, carbon nanotube etc. The ECP involves extremely conductive interconnects where metal particles are inserted within a polymer compound containing high temperature that are used for example bonding microprocessors and custom chip to PC boards. It can also reduce the use of expensive metals and increase reliability.

Current Development of Conducting Polymer as Textile Sensing Material

Conducting polymer materials are used in producing smart clothes including fiber/fabric-based triboelectric nanogenerators (TENGs) textiles. TENGs are developed using metal wires, conductive yarns or fiber-shaped elastomers that were coated with

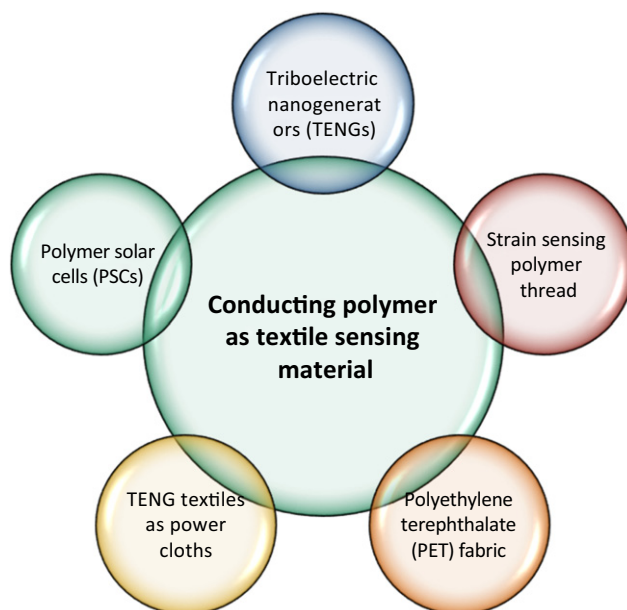


Fig. 4 Conducting polymers act as sensing material for smart textiles.

carbonaceous materials (Ren *et al.*, 2017). In addition, strain sensing polymer thread, (Sadeqi *et al.*, 2018) Polyethylene terephthalate (PET) fabric (Qiu *et al.*, 2019) and TENG textiles as power cloths are used as CP for making smart clothing. Fig. 4 provides some examples of conducting polymers used as the textile sensing material.

Triboelectric Nanogenerators (TENGs)

A strategy was proposed in Ren *et al.* (2017) for designing and fabricating triboelectric nanogenerators (TENGs) textiles based on fiber or fabric. Then the textiles were knitted from conductive silver-plated nylon threads using a knitting method which is available commercially. The TENGs are developed by employing either by fiber-shaped elastomers or conductive yarns which were coated with carbonaceous materials. Metal wires are also used to develop the TENGs. Dielectric polymer films such as polydimethylsiloxane (PDMS) were coated on fiber electrodes to act as triboelectrification layers. Then the customized either yarns or wires were hand-woven into the TENG textiles (Zhang *et al.*, 2016; Yu *et al.*, 2017a; Lai *et al.*, 2017; He *et al.*, 2017; Dong *et al.*, 2017; Chen *et al.*, 2016). TENG textiles are woven from conductive silver-plated nylon threads used as positive triboelectric material and charge collector using a knitting method which is available in the commercial market. An extended polytetrafluoroethylene (E-PTFE) membrane and ordinary fabric produced a laminated composite fabric combining with the textiles for realizing the TENG textiles. A portion of E-PTFE layer is attached over polyester fabric applying a heat-welding adhesive net. Then a thermal calendaring procedure was employed to produce the laminated fabric. The TENG textile, the laminated fabric samples, with other normal daily clothes were put in a commercial washing machine for 1 h and found steady while it is washed for ten times. However, the challenges of integrating TENG into textile fabrication processes and scaling up for mass production are yet to be addressed. The lightweight, washable and wearable TENG textiles can harvest energy from human activity to power for tiny electronics.

Strain Sensing Polymer Thread

The authors in Sadeqi *et al.* (2018) have fabricated stretchable and washable thread-based strain or force sensor which was stitched into the wearable textiles. Coating carbon resistive ink on a Polybutylene terephthalate (PBT) puffy thread was used to fabricate the sensor. A slim cover of polydimethylsiloxane (PDMS), skin compatible polymer was used to coat the carbon-coated thread. The thread was used to prevent flaking of carbon particles and for making it washable. PDMS is biocompatible and stretchable that creates the material appropriate for coating. It was observed that no significant changes in performances were found after several washing of the thread-based strain sensor using various cleansers. However, a negligible change in resistance was observed after washing repeatedly. Hydrophobicity of polymer makes it washable. The strain sensing fabrics is used for measuring human physiological motion.

Polyethylene Terephthalate (PET) Fabric

A washable power generation polyethylene terephthalate (PET) fabric has been created and presented in Qiu *et al.* (2019). Conductive fabric was used which is known as electrode attached on the behind of several fabrics and cutting into desired sizes in their work. To produce mechanical energy from human movement the fabric was then integrated with clothing. Electronegative organic

polymer materials such as polyvinylidene fluoride (PVDF) nanofibers (NFs) and polytetrafluoroethylene (PTFE) nanoparticles (NPs) were introduced on the surface of PET fabrics by using simultaneous electrospinning and electrospray techniques. Mechanical oscillator was used to wash the fabrics. After measuring and analysing the electrical output of the textile it was observed that output voltage and current stayed constant while the textile was washed for 2 hr. However, the electrical gain performance demonstrated slight degradation after washing the fabric for 12 h. The textiles observe human's activities and postures that are acted as a sensor of human movement. The fabrics also demonstrate tremendous breathability, flexibility and washability.

TENG Textiles as Power Cloths

TENG textile was used as power textiles, where primary shell yarns with basic conductive fibers acted as electrode and artificial polymer fibers was then rigidly bent across basic conductive fibers. Core shell yarns were consisted of stainless-steel (SS) fibers worked as main and dielectric fibers as the sheath. The core shell yarns then are woven into cloths. Dielectric materials for triboelectrification were served by the inner SS fibers linked together as the electrodes and the covering fibers. The washing test of the TENG textile was performed up to 120 times with a 5 h wash cycle to examine the stability of the textile. The washability and reliability of TENG textiles can be realized in fashionable garment designs and large-scale textile manufacturing. TENG textiles are also worn under the arm to monitor human motion including sitting, walking and running (Yu *et al.*, 2017b).

Polymer Solar Cells (PSCs)

A washable wearable display module with having self-powering ability was developed by the KAIST research team (Inavate, 2019). Polymer solar cells (PSCs) and organic light emitting diodes (OLEDs) were integrated with the module. A washable encapsulation obstacle was retained to protect the module by atomic layer deposition (ALD). Then a steam phase technique was applied to place thin films onto a layer of fabric. A spin coating procedure was applied to deposit uniform thin films to flat layers. Then the PSC, OLEDs and an encapsulation obstacle indicated a tiny change in characteristics while it is performed 20 washings with 10 min cycles. The display devices tested and found no deterioration in properties while it is bended and washed over a 30-day period. The technology can be used as a smart clothing for tracking fitness.

Researchers from Massachusetts Institute of Technology (MIT) has developed optoelectronic semiconductor-embedded washable fibers which is woven into soft fabrics with the use of light-emitting diodes (LEDs) and diode photodetectors (Tech Xplore, 2019). During drawing process, the fiber was heated in a furnace where polymer was melted to create a lengthy fiber with the diodes lined up along its center attached by the copper wires. The researchers washed the fabrics 10 times where photo-sensing fibers were placed in a tank full of water for a week and found that the functionality was retained. However, the fabric was not tested for washing more than 10 times. The fibers are utilized for communication and safety, lighting military applications, observing health parameters such as measurement essential statistics. It also monitors healing status through pulse meters and smart dressings.

Opportunity, Challenges and Future Development

Electrical and mechanical characteristics of a conducting fiber are dependent on the materials and their processing method. An Ashby plot in Fig. 5 shows a difference among electrical conductivity and Young's modulus of various forms of fibers and yarns. The plot is developed considering carbon fibers, carbon nanotubes, graphene, conjugated polymers. Polymers and materials associated with graphene exhibited superior conductivity compared to the carbon nanotube and carbon fibers. The most conducting and strongest fibers are positioned at the Ashby plot (top right corner) showing that additional conducting fibers seem to display a higher modulus (Lund *et al.*, 2018). For example, carbon nanotube and carbon fibers have high conductivity and higher stiffness. It is interesting to note that stiffness of the materials can vary by almost four orders of magnitudes and conductivity can vary by almost eight orders of magnitude. Therefore, a large number of material choices with huge varying range of properties are available to suit the requirements of sensor development and user comfortability. For example, to develop a resistive sensor, materials with lower conductivity can be preferred.

One of the major challenges of the smart clothing is to produce textiles in a scalable quantity with high durability of the fabric materials under repeated washing (Afroj *et al.*, 2019). Further development of the textile materials is required to make the clothes washable for longer period as most of the research works reported limited washability tests. Unstable metallic conductive fabric is also major concern while washing the clothes as the conductivity of the cloths is decayed after repeated washing (Afroj *et al.*, 2019). In addition, poor mechanical properties and processability are key obstacles for conducting fabric materials such as polymer to make the fabric washable (Wang *et al.*, 2019). Some materials are required encapsulation to make the clothes washable which is a big challenge as air permeability and moisture absorbency would be dropped due to the encapsulation. Besides, maintaining high electrical characteristics of printed tracks on the fabrics is challenging after washing. Further improvement in the accuracy of the sensors embedded in clothing can be achieved with the accurate selection of a mixture of materials capable of maintaining their conductivity and sensitivity after washing.

Washability of conducting polymer is an important fact among the above challenges. For example, the ranges of washability for some technologies compared to conducting polymers have been presented in Table 1. It is observed that carbon nanotubes and

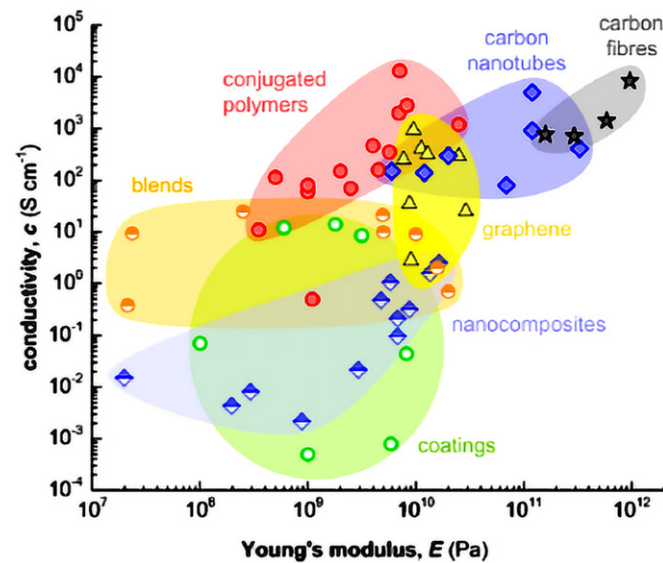


Fig. 5 Electrical conductivity vs. Young's modulus of fibers within polymers and other materials showed through Ashby plot. Reproduced from Lund, A., Velden, N., Persson, N., Hamed, M.M., Müller, C., 2018. Electrically conducting fibers for e-textiles: An open playground for conjugated polymers and carbon nanomaterials. *Mater. Sci. Eng. R* 126, 1–29.

Table 1 Washability testing ranges for smart fabrics based on different technologies

Name of technology	Washing time range	References
Graphene and other 2D materials	30 min to 2.5 h	Wang <i>et al.</i> (2019), Balandin <i>et al.</i> (2008), Novoselov <i>et al.</i> (2004), Geim (2009), He <i>et al.</i> (2012), Karim <i>et al.</i> (2017), Wearable technologies (2019), Carey <i>et al.</i> (2017), Huang <i>et al.</i> (2019), Montazerian <i>et al.</i> (2019), Fast Company and E-textile (2019), Thekkekara and Gu (2019), Yang <i>et al.</i> (2018), Karim <i>et al.</i> (2017)
Carbon nanotubes and nanofibers	2–40 h	Du <i>et al.</i> (2018), Cao <i>et al.</i> (2018), Hu and Zheng (2019)
Conducting polymers	30 s to 12 h	Ren <i>et al.</i> (2017), Zhang <i>et al.</i> (2016), Yu <i>et al.</i> (2017a), Lai <i>et al.</i> (2017), He <i>et al.</i> (2017), Dong <i>et al.</i> (2017), Chen <i>et al.</i> (2016), Sadeqi <i>et al.</i> (2018), Qiu <i>et al.</i> (2019), Yu <i>et al.</i> (2017b)
Semiconductor/microelectronic sensors	40 s to 10 min each day over 30 days	Gonçalves <i>et al.</i> (2018), Wang and Facchetti (2019), Cherenack <i>et al.</i> (2010), Seyedin <i>et al.</i> (2019), Kim <i>et al.</i> (2018), ETH <i>et al.</i> (2019), Abdelkader <i>et al.</i> (2017)

nanofibers-based technologies experimented the maximum washing length up to 40 h. Although graphene-based technologies are tested at lower range (30 min to 20.5 h) but the technologies are massively used by the researchers and increased user acceptability. Furthermore, graphene holds exceptional thermal conductivity among the other metals and carbon nanotubes (CNTs) (Balandin *et al.*, 2008).

Additional attempts on fabric materials should be given for constructing and designing system level device to realize extremely scalable smart clothing with washability capability like regular clothes would be appealing. By achieving longer washability of smart clothes along with high level of wearing comfortability and design flexibility, it is expected that the smart fabrics can be applied particularly in the area of medical surveillance, health monitoring and sports as the next-generation wearable products.

Now a days electronic product manufacturers are favouring towards flexible and miniaturization materials through development of microprocessors, actuators, sensors, etc. These vibrant technologies act as a fuel for the modernization in this field. This type of research can lead further development in the areas for example health observation, military and sports events, monitoring for vital indicators of life and injuries of human, and communication systems. Although many prototypes have already been developed as a trial basis in extreme environments and particularly clinical test experiments in the medical applications have also been begun. The enormous commercialization of some new developed product and ideas are still in progress and few of them have already been implemented however, there is still a lot of work to be accomplished to resolve all the technological issues. Fig. 6 shows the key technical challenges of conductive polymers materials for developing smart wearables.

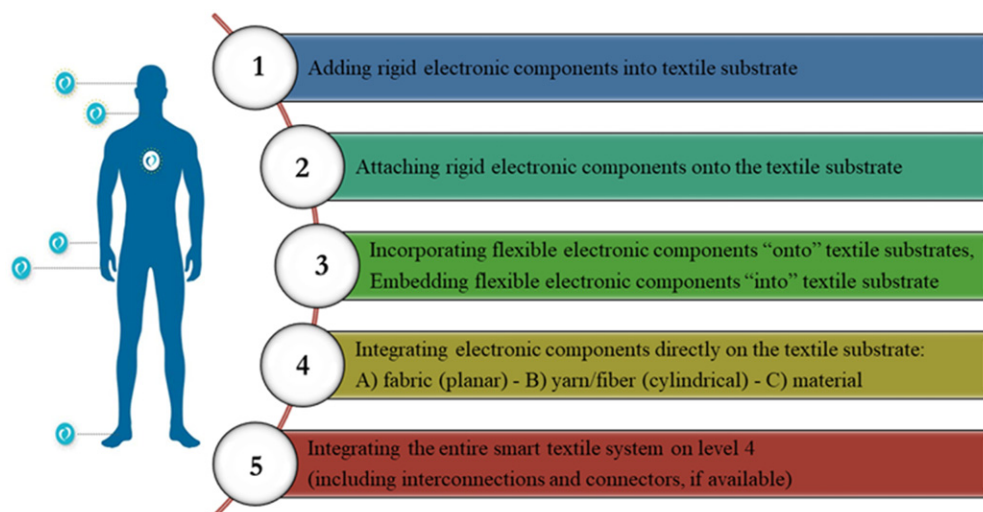


Fig. 6 Technical challenges of conductive polymer based materials for wearable device.

Conclusions

Sensors perform a key role in the areas of medical, safety, security and environmental diagnostics purposes worldwide. Conducting polymers are promising materials for developing the sensors for wearable technologies. The evolution of conducting polymer will open up designing various sensors and biosensors and their applications. The most common functionality of CPs is realised by designing appropriate polymer-based nanocomposites. Conducting polymer-based nanocomposites have also shown attractive characteristics where CP-based biosensors have shown the capability of solving the matters of biocompatibility for monitoring biological metabolites. Subsequently, the upcoming development into CP nanomaterials-based sensors can change the shape of future generation sensor-based products. Remarkably, it is predicted that suitable and flexible high-performance sensors will be developed through conducting polymer nanomaterials (Sołoducho and Cabaj, 2016b).

Further research on conducting polymer is still required from the stage of material to manufacturing of sensors and to integration with the fabrics to achieve commercialization level, with better accuracy, accessibility, service consistency, and cost effectiveness. For example, there is no further studies found for controlling uniformity at the stage of preparing and enhancing conductivity of PEDOT:PSS (Poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate)) solid films. Heterogeneity is another problem which is caused by phase separation when the drying process is conducted, that is required to solve when the PEDOT:PSS films are employed to high accuracy and metal-free products in near future. Great precision micro or nano processing utilized for PEDOT:PSS-based materials are costly and have limited yield. Thus, minimal cost and superior precision techniques should be introduced for bulk production in industry. PEDOT:PSS is responsive to temperature, humidity, where sufficient packaging and proper compensation can be introduced to develop PEDOT:PSS-based sensors. Polymer chain system of PEDOT:PSS-based hydrogels on the microscopic scale is another research direction in future to fully realize the microstructure of PEDOT:PSS-based hydrogels (Zhang *et al.*, 2021).

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Artificial Synapses Based On Two-Dimensional Materials

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Abstract

In the past, physical devices have approached the limit of Moore's law. The concept of neuromorphic computing was proposed to improve the processing efficiency. As one of popular materials with atomic-level thickness and fascinating properties, two-dimensional materials have been extensively researched for the implementation of synaptic device. This article will introduce two-dimensional materials-based artificial synapses from aspect of physical mechanism and neuromorphic characteristics.

Neuromorphic computing is a very large scale integration (VLSI) system which is used to mimic the activities of neuron and synapses in human brain (Mead, 1990).

The artificial synapse which emulates synaptic weight between two adjacent neurons is one of the key components in neuromorphic computing system. The characteristics of ideal artificial synapse generally include non-volatile synaptic weight, synaptic plasticity, low-power and compactness (Jiang *et al.* 2019).

Introduction

With the development of the society, the fast lifestyle needs a higher processing speed and results in the explosion of dataset size. Therefore, the demands for the computing ability and energy efficiency markedly increased day by day.

For information processing, the classical Von Neumann-based computing architecture is usually used for transferring the data between physically separated logic and memory blocks. When a huge amount of data becomes imperative to be handled, machine like human thinking is to be developed to undertake the complex tasks.

The human brain consists of $\approx 10^{12}$ neurons and $\approx 10^{15}$ synapses and consumes only 20 W when processing the different information. The synapses connecting two adjusted neurons can perform computation and memory simultaneously, which would break the Von Neumann bottleneck. Synaptic weight is defined as the connection strength between adjacent neurons. The concentrations difference of ionic species induces the change of synaptic weight (Bi and Poo, 1998; Schultz, 2001; Zucker and Regehr, 2002).

From the viewpoint of device physics, the ions can be regarded as the carriers which can be modulated by the external electric field. From this point, the concept of the neuromorphic computing has been developed to improve processing efficiency by mimicking the human brain's intelligence. Such neuromorphic computing can be realized by either software-based simulation or hardware-based circuit, respectively. The software-based approach always consumes a large amount of energy and space. In addition, the software-based simulation can't efficiently emulate parallel processing mechanism like brain because it is still realized by serial processing method in Von Neumann computer. The hardware-based approach for realizing neuromorphic computing is use synaptic devices to construct artificial neuron network, where the synapses are the physical conjunctions between neurons and the basic units for learning and computing like the human brain. Hence, hardware realization of synaptic function using solid-state device is a significant step for realizing the neuromorphic computing system.

Neuromorphic devices are categorized into multiple-terminal and two-terminal type. In the two-terminal synaptic devices, these two electrodes can be treated as presynaptic and postsynaptic terminals, respectively. In multiple-terminal synaptic devices, the gate electrodes can be considered presynaptic terminals and the drain/source electrode with the channel would be treated as postsynaptic terminal. Recently, the emerging low dimensional nanomaterials have attracted the growing interests due to the unprecedented electrostatic control (Jariwala *et al.*, 2017, 2013; Jariwala *et al.*, 2014; Kim *et al.*, 2017; Sangwan *et al.*, 2018). The atomically layered 2D materials have large specific surface area and super high sensitivity to external photoelectric signals, attracting the growing interests (Geim and Novoselov, 2007; Guo *et al.*, 2017; Jiang *et al.*, 2016a; Jiang and Dhar, 2016; Jiang *et al.*, 2016b; Novoselov *et al.*, 2005, 2004; Wang *et al.*, 2017; Zhang *et al.*, 2016), respectively.

As one of unique properties of 2D materials, the atoms are layered structures which are connected by van der Waals forces (Fig. 1). Owing to their layered nature, atomic thickness can be achieved to protect from the influence of interface defects, scattering and diffusion on device performance (Xia *et al.* 2014). In addition, uniform microstructure of 2D materials is benefit for realizing efficient control of gate electrode. In recent years, van der Waals heterostructures that stacks materials with different dimensional provide a new possibility in realizing photoelectric detector with wider detection range, becoming a new research hotspot in 2D materials applications (Kang *et al.*, 2016; Wen *et al.*, 2016). Due to diverse optoelectronic and morphological properties of 2D materials, artificial synapses based on 2D materials can simultaneously perform sensor and memory function to external stimuli with high power efficiency, which is benefit for realizing biological sensory-perception systems. In this article, neuromorphic characteristics and physical mechanism of 2D materials based-artificial synapses will be introduced.

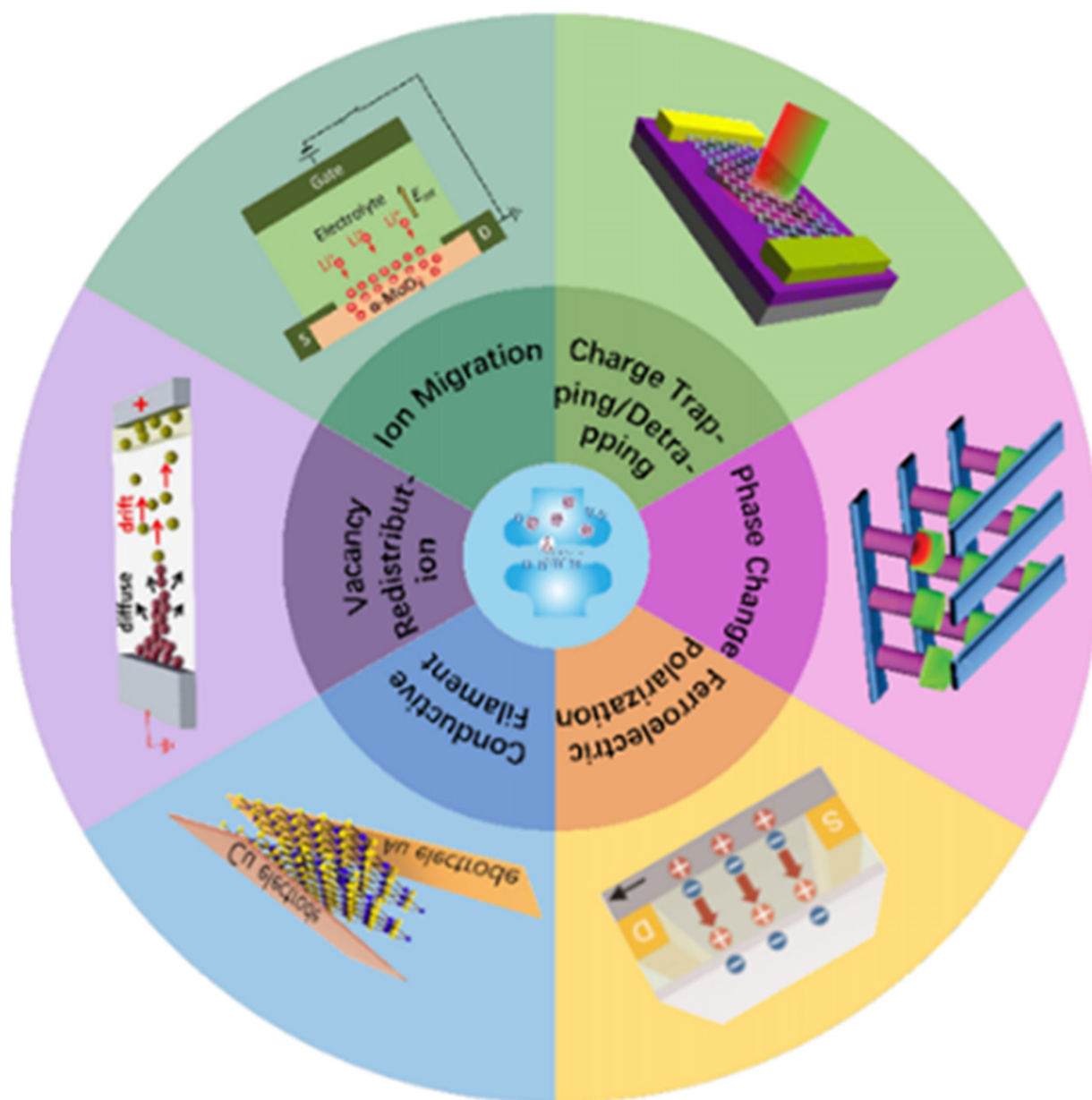


Fig. 1 A pi chart of some synaptic devices based on 2D materials. Reproduced from Chen, Y., Zhou, Y., Zhuge, F., *et al.*, 2019. Graphene-ferroelectric transistors as complementary synapses for supervised learning in spiking neural network. *Npj 2d Materials and Applications* 3. Kuzum, D., Jeyasingh, R.G.D., Lee, B., Wong, H.S.P., 2012. Nanoelectronic programmable synapses based on phase change materials for brain-inspired computing. *Nano Letters* 12 (5), 2179–2186. Qin, S., Wang, F., Liu, Y., *et al.*, 2017. A light-stimulated synaptic device based on graphene hybrid phototransistor. *2d Materials* 4, 3. Xu, R., Jang, H., Lee, M.-H., *et al.*, 2019. Vertical MoS2 double-layer memristor with electrochemical metallization as an atomic-scale synapse with switching thresholds approaching 100 mV. *Nano Letters* 19 (4), 2411–2417. Yang, C.-S., Shang, D.-S., Liu, N., *et al.*, 2018. All-solid-state synaptic transistor with ultralow conductance for neuromorphic computing. *Advanced Functional Materials* 28, 42. Zhu, X., Lu, W.D., 2018. Optogenetics-inspired tunable synaptic functions in memristors. *ACS Nano* 12 (2), 1242–1249.

Biological Synapses and Synaptic Properties

Synapses can realize switching between electric signal and chemical signal, and transmit information between different neurons by the migration of neurotransmitters. The biological synapses contain electrical synapses and chemical synapses (Fig. 2). The chemical synapses are playing an important role in learning and memorizing (Pereda, 2014). When external electrical signals arrive at the presynaptic membrane and reach the threshold value of action potential, the Ca^{2+} channels will open. The neurotransmitters would be released to the synaptic cleft, binding with receptors in the post synapses. Therefore, it will finally open the ion channels and change the potential of postsynaptic membrane according to the type of neurotransmitters. Generally, the ions are Na^+ , Cl^- and K^+ whose

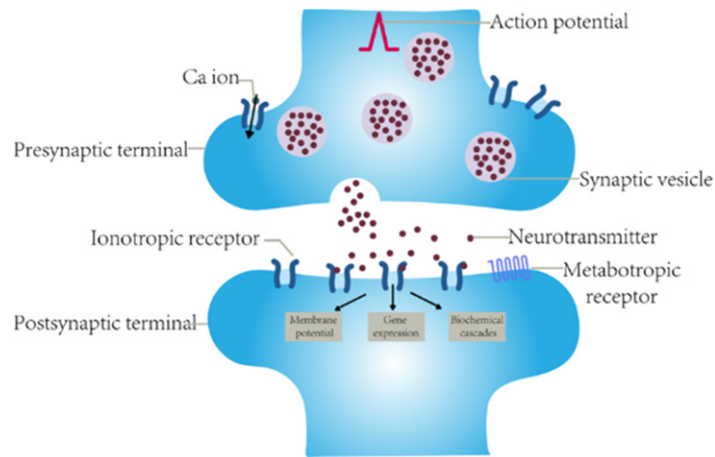


Fig. 2 Chemical synapses.

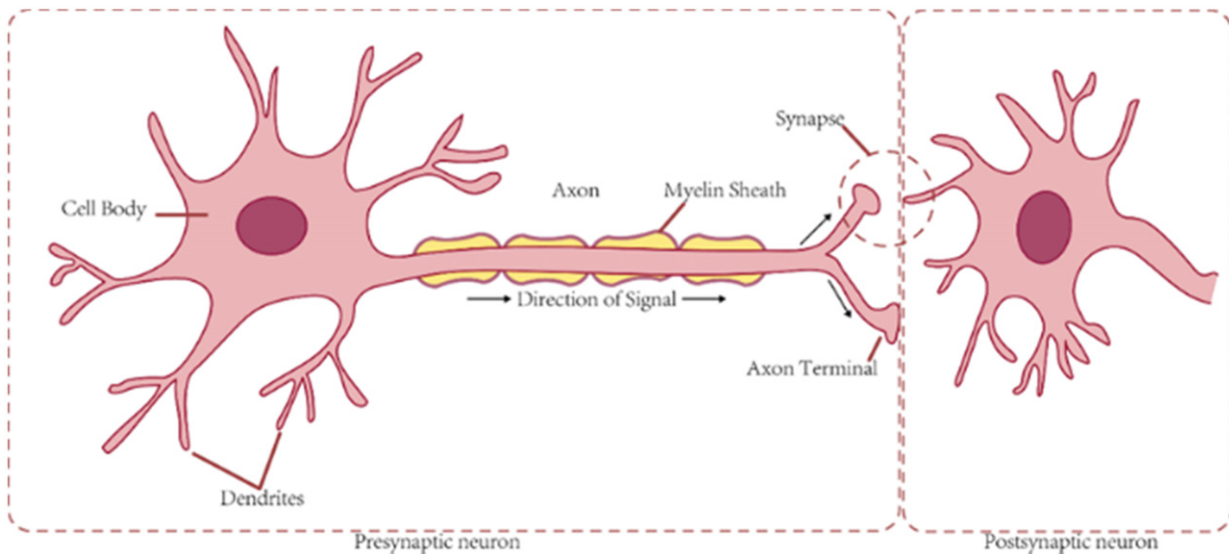


Fig. 3 The structure of biological neuron.

concentration gradients are separately distributed (Mayford *et al.*, 2012; Pereda, 2014). K ions are concentrated within neurons, whereas Na ions and Cl ions are more focused in extracellular medium (Park *et al.*, 2020). The ion concentration difference between intracellular and extracellular mediums induces potential difference. The potential of extracellular medium is usually larger than that in intracellular. The potential difference is about -70 mV which is called as the resting potential (Lewis *et al.* 2011).

Excitatory/Inhibitory Postsynaptic Potential/Current

In excitatory synapses, the membrane potentials become depolarized by Na⁺ influxes. The change of potential is called as excitatory postsynaptic potential (EPSP) (Ferster and Jagadeesh, 1992, Schultz, 2001), while the change of current is called as excitatory postsynaptic current (EPSC) (Schultz, 2001). As a contrast, the membrane potentials of inhibitory synapses become hyperpolarized by Cl⁻ influxes. The change of potential is called as inhibitory postsynaptic potential (IPSP) (Ferster and Jagadeesh, 1992), while the change of current is called as inhibitory postsynaptic current (IPSC) (Schultz, 2001).

Dendrites Integration

The dendrites can collect, integrate and modulate presynaptic signals from different presynaptic terminals, finally transmitting these signals to postsynaptic neurons through axons (Fig. 3). The dendrite integration can be performed using both the spatial and temporal approaches (Wigge *et al.*, 2005). The spatial integration is addition of the events which occurs simultaneously in different regions, while the temporal integration is addition of non-simultaneous unitary events (Branco and Hausser, 2010; Krueppel *et al.*, 2011). The sub-linear (super-linear)

integration (Hines and Carnevale, 1997) occurs when the combined response of multiple inputs is less (more) than the sum of individual response.

Synaptic Plasticity

It has been reported that synaptic plasticity is the basic of learning and memorizing in human brain, which is synaptic weight changes with the action potential (Mayford *et al.* 2012, Zucker and Regehr, 2002). According to the retention time, it can be divided into short-term plasticity and long-term plasticity. The short-term plasticity lasts for tens of milliseconds and always activated by temporary events, which contains facilitation, depression and potentiation state. As a contrast, the long-term plasticity lasts from few minutes to a lifetime, containing facilitation, depression and potentiation state, respectively. When the duration or the frequencies of train process is large enough, the concentration of Ca^{2+} will increase and gradually exceed the threshold, finally inducing the synthesis of the Ribonucleic Acid (RNA) which contains the important information (proteins) to construct a new synapse (Kakegawa and Yuzaki, 2005, Riedemann *et al.* 2010). When the presynaptic spikes with low frequency are applied, the number of neurotransmitters will decrease, which can be called as the long-term depression (Riedemann *et al.* 2010, Weber *et al.* 2003).

Paired-Pulse Facilitation

The representatives of short-term plasticity are the paired-pulse facilitation (PPF) and paired-pulse depression (PPD). The PPF underlie decoding temporal audiovisual information (Schultz, 2001). To demonstrate the extent of the facilitation, the PPF index can be defined as: $A_2/A_1 \times 100\% = \text{PPF index}$, where A_1 and A_2 are the peak of EPSC for the first and the second spikes, respectively. When time spacing between two presynaptic spikes is shorter than the relaxation time that ions are entirely back to the initial state, all of ions that triggered by the first spike can't timely relax to the equilibrium state. Therefore, these residual ions cause the addition of ions that triggered by the next stimuli, finally resulting the second response (EPSC) is larger than the previous one. As previously mentioned, the PPF index changes with the time interval between the two presynaptic signals. The minimum value of PPF index is 100% when the second EPSC is the same as the first one, i.e., PPF phenomenon is disappearing. The second EPSC is smaller than the first one, which is called as PPD. The depression of synaptic weight plays an important role in perceptor adaptation, sound localization and improvement of information processing efficiency (Fortune and Rose, 2000).

Memory

Human memory contains sensory memory (SM), long-term memory (LTM) and short-term memory (STM). Repeatable and long-duration train enables the transition from STM to LTM (Riedemann *et al.* 2010). In the human brain, the information are encoded as electrical spikes with different amplitudes. The parameters of the electrical spike mainly modulate the synaptic plasticity, finally complete the process of learning and memorizing (Martin *et al.* 2000, Mayford *et al.* 2012, McGaugh, 2000).

Spike-Rate Dependent Plasticity

Spike-rate dependent plasticity (SRDP) is defined as the change of synaptic plasticity according to the frequency of the stimuli (Dudek and Bear, 1992, Markram *et al.* 1997, O'Dell and Kandel, 1994). When the frequency of input exceeds certain threshold, the synaptic weight would potentiate for a long time, or it would depress. In other words, the synaptic weight will present long-term potentiation (depression) under the presynaptic spike with high (low) frequency.

Spiking Timing-Dependent Plasticity

In 1949, Hebb *et al.* proposed that the arrival time of postsynaptic spike would influence the synaptic weight. As research of biological neuron network further develops, the learning rule and synaptic activities become more comprehensive. Bi and Poo have proposed spiking timing-dependent plasticity (STDP) (Bi and Poo, 1998). The effect of STDP is exhibited in equation 1 using a simple exponential.

$$\Delta w = A e^{\frac{-\Delta t}{\tau}} \quad (1)$$

where Δw is the relative change in synaptic weight, Δt is the time spacing between presynaptic and postsynaptic spikes. τ correspond to the time constant for STDP curve, which exhibits significant variation according to the location of the synapses in the brain (Bi and Poo, 2001, Froemke and Dan, 2002, Levy and Steward, 1983, Pratt *et al.* 2008, Wittenberg and Wang, 2006).

As a learning rule of the brain, STDP has completed the Hebbian learning rule. Time difference $\Delta t = t_{\text{pre}} - t_{\text{post}}$, where t_{pre} and t_{post} are the arrival time of the presynaptic and postsynaptic spikes, respectively. When presynaptic spike arrives after postsynaptic spike ($\Delta t > 0$), the synaptic weight would potentiate, otherwise the depression would occur ($\Delta t < 0$). When these two spikes arrive at the same time ($\Delta t = 0$), the magnitude of the EPSC would increase to maximum value.

The biological synapses with different functionalities exhibit different forms of STDP (Wittenberg and Wang, 2006). The symmetric STDP enables robust sequence learning (Hayashi and Igarashi, 2009). The synaptic weight in asymmetrical STDP is modulated by the synergetic effect of time interval and timing sequence, while the symmetrical STDP is only relevant to the time interval (Dan and Poo, 2004, Maistrenko *et al.* 2007, Mishra *et al.* 2016) (Fig. 4).

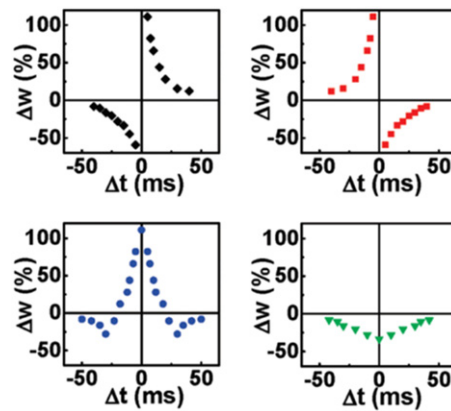


Fig. 4 Two types of asymmetrical STDP (upper) and two types of symmetrical STDP (lower). Reproduced from Kuzum, D., Jeyasingh, R.G.D., Lee, B., Wong, H.S.P., 2012. Nanoelectronic programmable synapses based on phase change materials for brain-inspired computing. *Nano Letters* 12 (5), 2179–2186.

Dynamic Filter in Biological Synapses

Since synapse plasticity is efficacy variation during synaptic transmission (Fortune and Rose, 2000, Schultz, 2001), the synapse can be regarded as a dynamic filter. The biological synapses would exhibit properties like high/low pass filter according to the frequency of signal during synaptic transmission. The signal with higher frequency induces greater potentiation of synaptic weight, finally generating stronger output, which is somewhat alike to high pass filter.

Physical Mechanism

Two-Terminal Artificial 2D VdW Synapses

In recent years, as a novel neuromorphic device, memristor has been extensively researched due to its nonlinear characteristics in updating synaptic weight. This concept was proposed by Leon O. Chua in 1971s when he was investigated the relationship among charge, current, voltage and magnetic flow (Chua, 1971). However, its physical prototype device didn't find until HP Laboratory reported it in 2008 (Strukov et al. 2008). As a candidate for emulating biological synapse, the resistance of memristor changes with the applied current/voltage, which is kept in a non-volatile way. Two-terminal synaptic devices like memristors have two metal electrodes and an electrolyte between them, storing or changing synaptic weight in photoelectric synergy approach. Both read and write operations are finished by sharing a common terminal in two-terminal synaptic device. Insufficient effective conductance state and small dynamic range are obstacles for implementation of artificial neuron network with such two-terminal synaptic devices. However, from the perspective of fabrication, such two-terminal neuromorphic devices have good scalability due to the crossed point array. Next, two-terminal 2D VdW synaptic devices that have developed by formatting conductive filament, redistributing vacancy, charge trapping/de-trapping and phase changing, respectively, will be introduced.

Conductive filament formation

Just-completed resistive random devices are usually exhibit high resistance state (HRS). However, the devices will be soft breakdown to the low resistance state (LRS) under the applied forming voltage, this process is called as forming. When the forming process is finished, conductive filaments will form in the resistive random layer to connect these two electrodes. Therefore, the resistive random device becomes LRS. The conductive filament-based two-terminal synaptic devices updating and storing weight through the formation and deformation of conductive filaments. Conductive filaments are usually formed by the motion of the cations that origin from the electrochemical material (Lee et al. 2018, Lv et al. 2015, Onofrio et al. 2015, Shi et al. 2018, Xu et al. 2019).

Xu et al. (2019) reported a memristor with active copper (Cu)/two molybdenum disulfide (MoS_2) monolayers/inertia gold (Au) vertical structure (Fig. 5(a)). The two MoS_2 monolayers exhibit bipolar and analogous resist switching behavior. On the either polarity of applied voltage, the memristor exhibits two states which are HRS and LRS, respectively, while it can't simultaneously accomplish both set and reset process (Fig. 5(b)). As the applied voltage increases, Cu ions that are oxidation results of Cu electrode flowing cross the MoS_2 layers, then be reduced and electrical deposited by the bottom Au electrode. As increasing number of Cu ions that accumulate on the bottom electrode, the conductive filaments are forming to bridge the two electrodes, gradually increasing the conductance of MoS_2 monolayers. Therefore, the device finally set as LRS. To reset device, the voltage with opposite polarity is applied to collect Cu ions in the MoS_2 layers. As result, the conductivity of MoS_2 layers gradually reduces and then contributes to the reset of the device (HRS). It should be noted that the two electrodes are also bridge conductive filaments in HRS, while the cross-section area of conductive filaments of device in HRS is smaller than that in LRS (Fig. 5(c)). STDP with low switching voltage was demonstrated in this device as the first one among the 2D materials-based memristors with vertical structure.

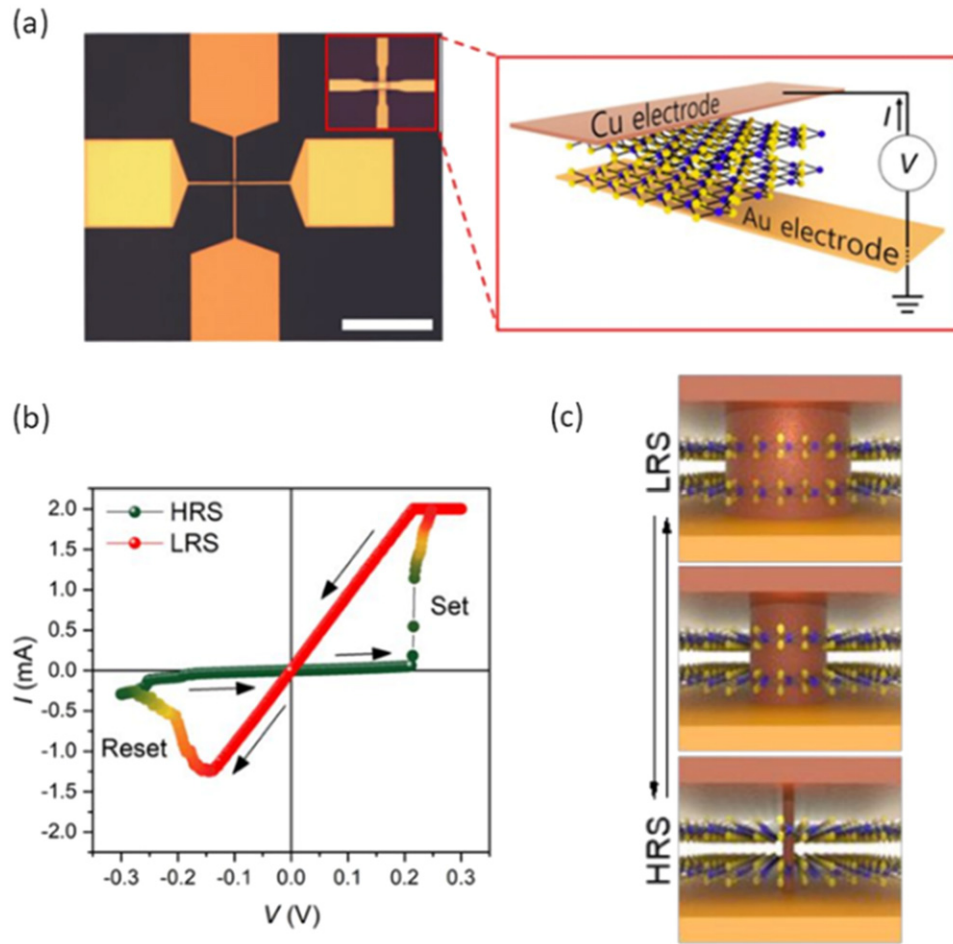


Fig. 5 MoS₂ vertical memristor. (a) An optical image of the proposed device. (b) I-V sweeping curve at input voltage ranging from -0.3 – 0.3 V. (c) The transition process between LRS and HRS. Reproduced from Xu, R., Jang, H., Lee, M.-H., *et al.*, 2019. Vertical MoS₂ double-layer memristor with electrochemical metallization as an atomic-scale synapse with switching thresholds approaching 100 mV. *Nano Letters* 19 (4), 2411–2417.

Shi *et al.* fabricated some memristors with fixed middle layer material of hexagonal Boron Nitride (h-BN) (Shi *et al.* 2018). The sharp of I-V sweeping curve and break-down voltage markedly changed when different top electrode materials were used, which effectively confirmed that the conductive filaments were formed by cations origin from the electrode and that penetrate into the h-BN layers under external stimuli.

Lee *et al.* developed a Ag/ chromium thiophosphate (CrPS₄)/Au capacitor vertical structure to emulate biological synapse (Lee *et al.* 2018). A layered CrPS₄ single crystal was used as electrolyte layer, which shows the same properties as cuprous sulfide (Cu₂S). To figure out the influence of the thickness of CrPS₄ on device performance, two devices with different CrPS₄ thickness were used. The thicker one exhibits the lower HRS current and more abrupt resist switching behavior (larger on/off resistance ratio). The thicker one needs a larger voltage to form a conductive filament, when compared with the thinner one. Some essential synaptic functions were also demonstrated, such as synaptic plasticity, transition between long-term plasticity and short-term plasticity.

Vacancy redistribution

In the semiconductor/mental interface, vacancy redistribution can be controlled by the external photoelectric signal, and result in the change of channel conductance by modulating interface Schottky barrier (Le *et al.* 2014, Li *et al.* 2018, Sangwan *et al.* 2018, Zhu and Lu, 2018).

Li *et al.* (2018) investigated the switching property of MoS₂ memristor with planar structure (Fig. 6(a, b)). Two direct-current (DC) programming switching patterns were found, which were rectification mediated pattern and conductance mediated pattern, respectively. Rectification mediated pattern can be attributed to the change of MoS₂/ Titanium (Ti) interface Schottky barrier. To verify above mentioned mechanism, a hypothesis was proposed, in the case of sulfur vacancies migrate to the Ti/gold (Au) contact under external electrical field, the result of the increase in Ti/ MoS₂ interface Schottky barrier contributes to the decrease of channel conductance. Three qualitative device models were proposed to describe the rectification mediated pattern, confirming the hypothesis. The rectification ratio of the Schottky diode in the models was symbolized by the size of diode (Fig. 6(c-f)). Due to the conductance mediated patten with low switching ratio is unsuitable for implementation of HW-NNs, it is necessary to realize transition from conductance mediated pattern to rectification mediated pattern. Two solutions were proposed: shortening the

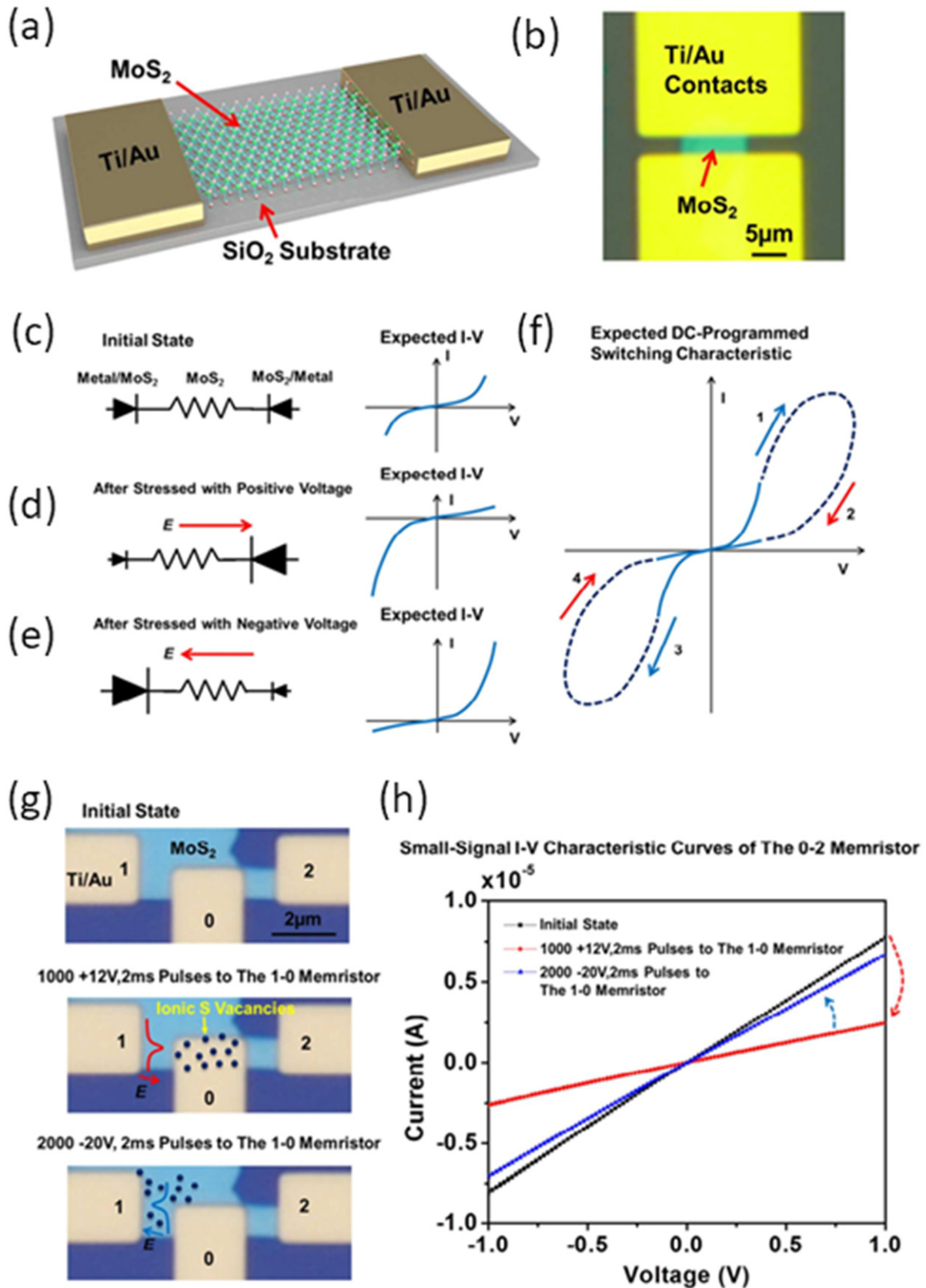


Fig. 6 A few-layer MoS₂ memristor exhibiting variable switching characteristics. (a) A schematic diagram of proposed MoS₂ memristor. (b) An optical image of proposed memristor. Qualitative device models are listed in (c)(d)(e), (c) initial state, (d) backward-diode state, (e) forward-diode state. (f) Idea switching characteristics with DC-programmed. Simulation of biologically ionic coupling is illustrated in (g) and (h), (g) the migration of ionic sulfur vacancies under external electrical field. (h) Small-signal I-V curves of the memristor that was labeled with 0-2. Reproduced from Li, T., Lipatov, A., Lu, H., *et al.*, 2018. Optical control of polarization in ferroelectric heterostructures. *Nature Communication* 9 (1), 3344.

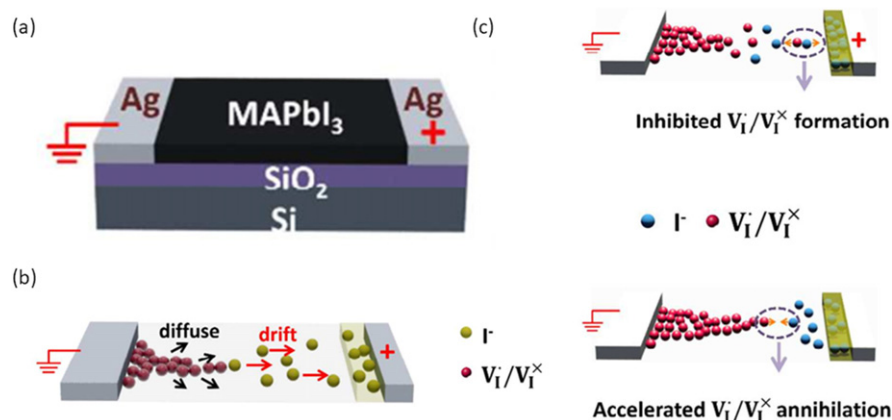


Fig. 7 A planar memristor based on CH₃NH₃PbI₃(MAPbI₃). (a) A schematic image of this device. (b) The creation and diffusion of iodine vacancy V_I/V_I^x. (c) The influence of light stimuli on formation of V_I/V_I^x under electric bias. Reproduced from Zhu, X., Lu, W.D., 2018. Optogenetics-inspired tunable synaptic functions in memristors. ACS Nano 12 (2), 1242–1249.

channel length and expanding the DC voltage sweep range. Two adjacent MoS₂ memristors were integrated to mimic biologically ionic coupling. The applied programming voltage in one memristors controlled the sulfur distribution around the common Schottky junction, modulating the state of the other memristor (Fig. 6(g, h)).

Zhu *et al.* developed a planar memristor based on CH₃NH₃PbI₃(MAPbI₃) (Zhu and Lu, 2018) (Fig. 7(a)). The iodine vacancies in MAPbI₃ function as the neurotransmitters. Optical signal increases the format energy of the iodine vacancy, accelerating annihilation as well as inhibiting formation, finally resulting a decrease in channel conductance. As a contrast, under electrical stimulation, with increasing concentration of the iodine vacancy in the MAPbI₃ film, the channel conductance gradually increases. (Fig. 7(b, c)). Both coincidence detection and enhancement of memory can be emulated by optoelectronic synergy stimulation.

Charge trapping/de-trapping

The trapped/de-trapped carriers in the mental/semiconductor interface can change channel conductance of synaptic device, resulting the potentiation/depression of synaptic weight (Kumar *et al.* 2019, Vu *et al.* 2016, Yan *et al.* 2019).

For achieving faster switching speed, Yan *et al.* (2019) presented a low-power memristor based on tungsten disulfide (WS₂) with 2 H phase. Platinum (Pt) and palladium (Pd) materials were used as ground and positive electrodes, respectively (Fig. 8(a)). The basic synaptic functions were successfully mimicked in this memristor, such as PPF (Fig. 8(b)) and STDP (Fig. 8(c, d)). The calculation about tunneling current and transmission probability based on conductance theory of trap-assisted tunneling (TAT) mechanism were performed to investigate physical principle of the memristor. The testing I-V curves were well fitted with above mentioned theory equations, which confirmed that the dominant role of TAT in this memristor. The applied voltage increases Joule heating to drive the lighter atoms (sulfur atoms and tungsten atoms) away from their original location.

Phase changing

Phase change materials could switch between amorphous and crystalline states under the applied heat signal in optoelectrical approach. Phase change memory (PCM) has been extensively researched due to the unique advantages, such as fast operation speed and scalability. Chalcogenide alloy materials is a class of phase change materials. Among them, Ge₂Sb₂Te₅ (GST) is considered to be the most suitable for being phase change material (Ovshinsky, 1968, Raoux, 2009, Wuttig and Yamada, 2007). Over the years, many PCM structures have been proposed, two of them have been well acknowledged (Banerjee, 2020): mushroom sharp structure (more representative) and linear structure. The mushroom sharp structure is advantageous for the direct contact between phase change materials and resistance/heater, resulting a large reduction in heat loss. The heater is usually made from resistant materials with thermostability and chemical inertness, such as tungsten. When the voltage is applied on PCM, the heat which generated by resistance transmits to the phase change materials, facilitating the phase changing process. PCMs can be reversibly switched among intermediate conductance states under applied photoelectrical pulses, which make it is possible to emulate a variety of synaptic functions (Boybat *et al.* 2018, Chhowalla *et al.* 2013, Gong *et al.* 2017, Hong *et al.* 2016, Jung *et al.* 2016, Kuzum *et al.* 2012, Sun *et al.* 2016, Wang *et al.* 2014, Zhu *et al.* 2018).

A two-terminal synaptic device where the GST was used as a functional layer was proposed (Kuzum *et al.* 2012) (Fig. 9(a)). The tungsten which capped with Titanium Nitride (TiN) and TiN were used as top and bottom electrodes, respectively. By changing parameters of the electric pulses (Fig. 9(c)), well controlled of the time constant of the STDP is obtained, which is benefit for implementing more complex cognitive function in artificial synapse. The large reset voltage facilitates the amorphous state of GST. A large mushroom sharp which is characteristic of the amorphous volume (Fig. 9(b)) shows on the top of the bottom electrode, blocking the carriers flow through middle layer. Finally, the device presents in the fully reset state, which characteristics in the large resistance. On the contrary, the set voltage induces the polycrystalline state of GST. The temperature of amorphous region that increased by the applied set voltage finally exceeds crystallization temperature, inducing an increase in conductance with

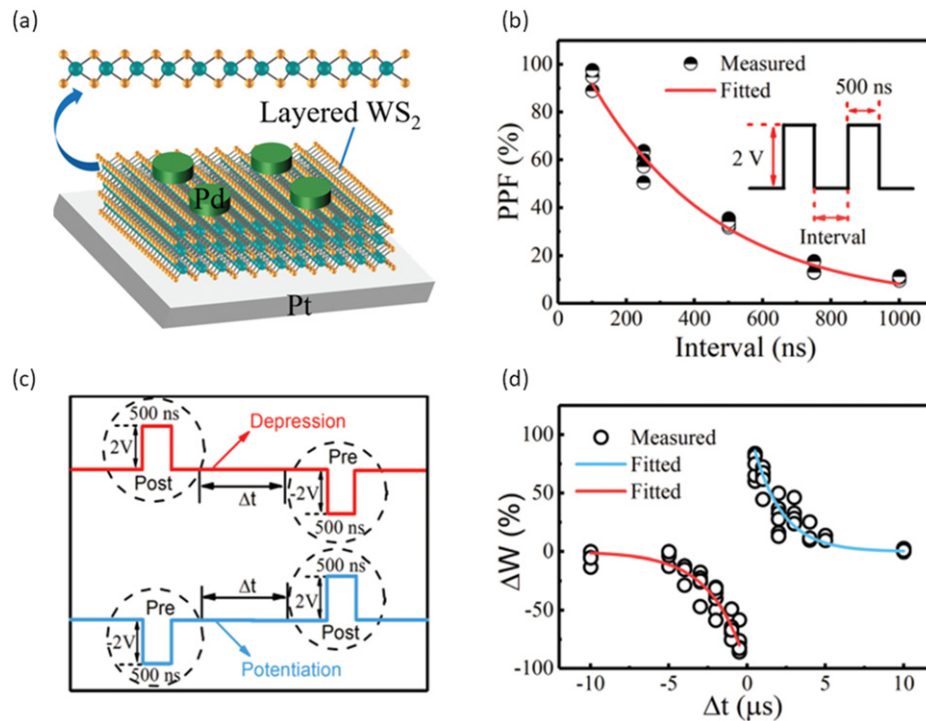


Fig. 8 A WS₂ nanosheet-based memristor realizing PPF and STDP. (a) Schematic illustration of proposed device structure. (b) The PPF curve. (c) The electrical voltage setting for testing STDP. (d) STDP curve. Reproduced from Yan, X., Zhao, Q., Chen, A.P., *et al.*, 2019. Vacancy-induced synaptic behavior in 2D WS₂ nanosheet-based memristor for low-power neuromorphic computing. *Small* 15 (24), e1901423.

appearance of crystalline state. To progressively change amorphous region into crystalline state, the voltage pulses with gradually increasing number are applied. Therefore, well control of multiple conductance states can be achieved. The presented two-terminal artificial synapses exhibited ultralow femtojoule energy consumption and fast operation speed using phase change materials.

Tuma *et al.* proposed a novel non-differential architecture based-multi-memristive synapse (Boybat *et al.* 2018). Such synaptic device mitigated the partial significant challenges of the memristor in the implementation of artificial neuron network. In the non-differential architecture, every synapse comprises more than one device to achieve synaptic plasticity. Interestingly, device is selected to be potentiated/depressed one by one, inducing gradual change of conductance. Therefore, the dynamic range of effective conductance state promotes with the number of devices that construct one synapse. In addition, the impact of such multi-memristive synapse on artificial neural networks and spiking neural networks was investigated by classifying handwritten digit. The classification accuracy promotes as the number of devices increase, exceeding 88.9% which better than other phase change material-based two-terminal synaptic devices.

Three or Multiple Terminals Artificial 2D VdW Synapses

Due to their simple structure, low volume and high-device-integration, these two-terminal synaptic devices have been extensively researched as one of promising base elements of artificial neural networks (Prezioso *et al.* 2015, Xu *et al.* 2016).

Nevertheless, the data transfer and learning can't simultaneously be performed in these devices, which blocks its further application in the advanced neuromorphic engineering (Nishitani *et al.* 2012). Three-terminal or multiple-terminal devices are not only overcoming the shortcoming of two-terminal devices but also possessing unique advantages such as high stability, flexible structure, clear mechanism and multi-parameter (Zhu *et al.* 2014). Three-terminal or multiple-terminal devices can convert external stimuli (for instance, light, temperature, pressure) to electrical signals, directly responding external environment (Dai *et al.* 2018, Wang *et al.* 2019). Furthermore, the biological dendrite integration and parallel learning which need multiple terminals can be easily realized in the multiple-terminal synaptic devices, which is helpful for achieving neuron network with less synaptic device. Hence, the three-terminal or multiple-terminal synaptic devices are more appropriate to emulate synaptic functions than two-terminal devices.

Charge trapping/de-trapping

To potentiate or depress the conductivity of semiconductor, the trapped or de-trapped charges contributes to the retention time of trapping state by changing the width of the tunneling barrier between the electrode and the channel under external electrical field (Fan *et al.* 2020, Jayachandran *et al.* 2020, Qin *et al.* 2017, Tian *et al.* 2016, Yu Jeong Park 2018, Zhu *et al.* 2018).

To mimic the escape response of locusts, Jayachandran, D.*et al.* proposed a biomimetic MoS₂-based collision detector (Jayachandran *et al.* 2020) that utilized threshold voltage engineering ability of floating gate and photoresponsivity of MoS₂. The detector compromises

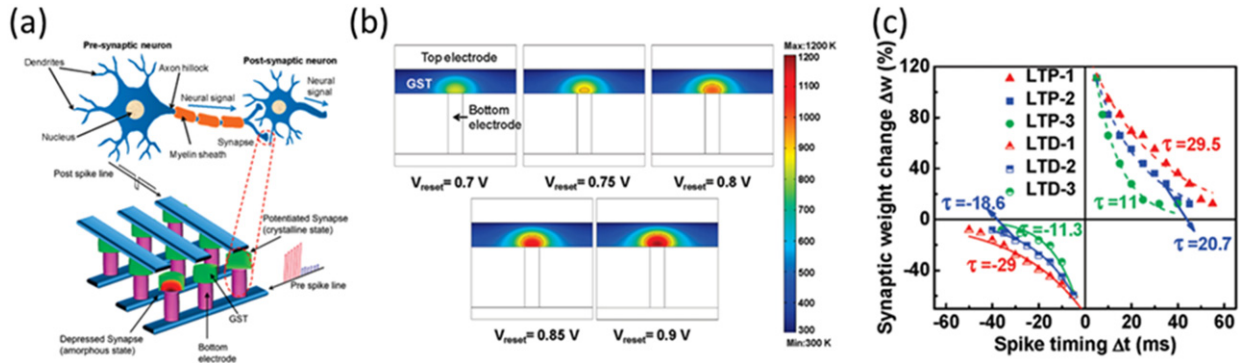


Fig. 9 A programmable synapse based on GST for neuromorphic computing. (a) Crossbar array using PCM synapses is illustrated. (b) Finite element simulations are shown. (c) STDP response with different time constants. Kuzum, D., Jeyasingh, R.G.D., Lee, B., Wong, H.S.P., 2012. Nanoelectronic programmable synapses based on phase change materials for brain-inspired computing. *Nano Letters* 12 (5), 2179–2186.

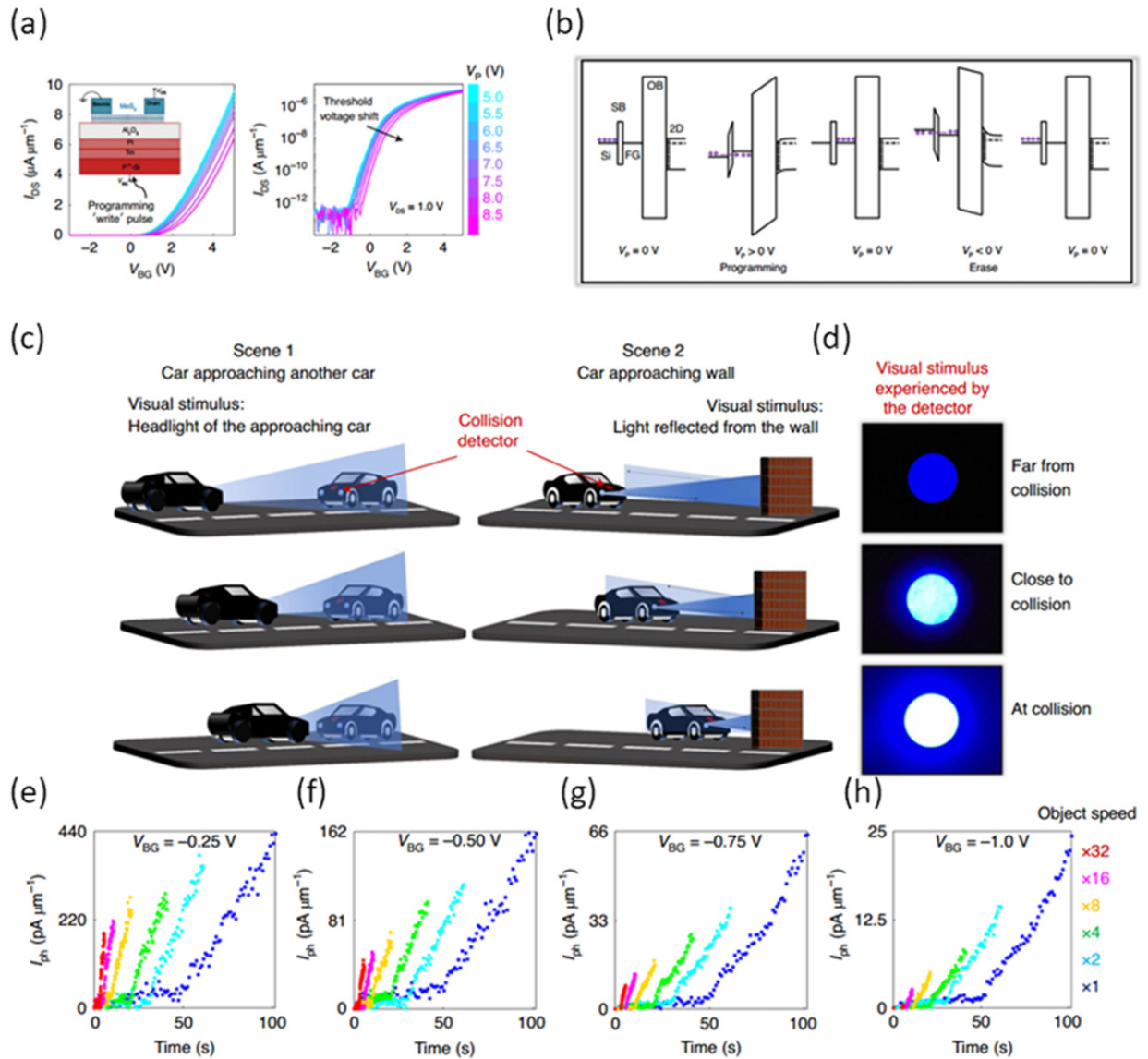


Fig. 10 MoS₂ based-biomimetic collision detector. (a) Transfer curve in linear (left) / logarithmic (right) scales after application of programming pulse. (b) Energy band diagram about programming and erase process. (c) The direction collision process of two cars. (d) The light density is growing as the instance is closing. (e–h) The photoresponse of MoS₂ transistor under different back gate bias, (e) – 0.25 V, (f) – 0.5 V, (g) – 0.75 V, (h) – 1.0 V. Reproduced from Jayachandran, D., Oberoi, A., Sebastian, A., *et al.*, 2020. A low-power biomimetic collision detector based on an in-memory molybdenum disulfide photodetector. *Nature Electronics* 3 (10), 646–655.

monolayer MoS₂ photodetector and a floating-gate with aluminum oxide (Al₂O₃)/Pt/TiN/P⁺⁺-Si structure (Fig. 10(a)). The large positive back gate voltage induces that holes in the P⁺⁺-Si flowing into Pt/TiN floating gate and be trapped (Fig. 10(b)). The trapped holes mirror electrons on the top of floating gate and decrease the concentration of major carriers in the MoS₂ channel. Hence, output current (I_{DS}) would decrease in the dark (no collision possibility situation). Meanwhile, threshold voltage is increases with bottom gate voltage, resulting the inhabitation in output. On the contrary, due to the excellent photoresponsivity of MoS₂, I_{DS} would increase when there is reflected light or light from collision object (Fig. 10(c, d)). It is possible to enhance light sensitivity by optimizing gate bias (Fig. 10(e-h)). When electrical inhabitation and light excitation are simultaneously present, the non-monotonic trend of output signal is the same as the escape response of locust, which successfully emulates the LGMD neuron function in the locusts.

Y. J. Park *et al.* proposed a 3D stacked synapse array Yu Jeong Park *et al.* (2018). To implement synaptic plasticity, the operation methods were designed as hot-electron injection and hot-hole injection, respectively. A positive drain voltage pulse that combines with positive gate voltage induces the hot-electron injection, to decrease the channel conductance and increase threshold voltage. On the contrary, the hot-hole injection increases the conductance and decreases threshold voltage by applying the positive drain

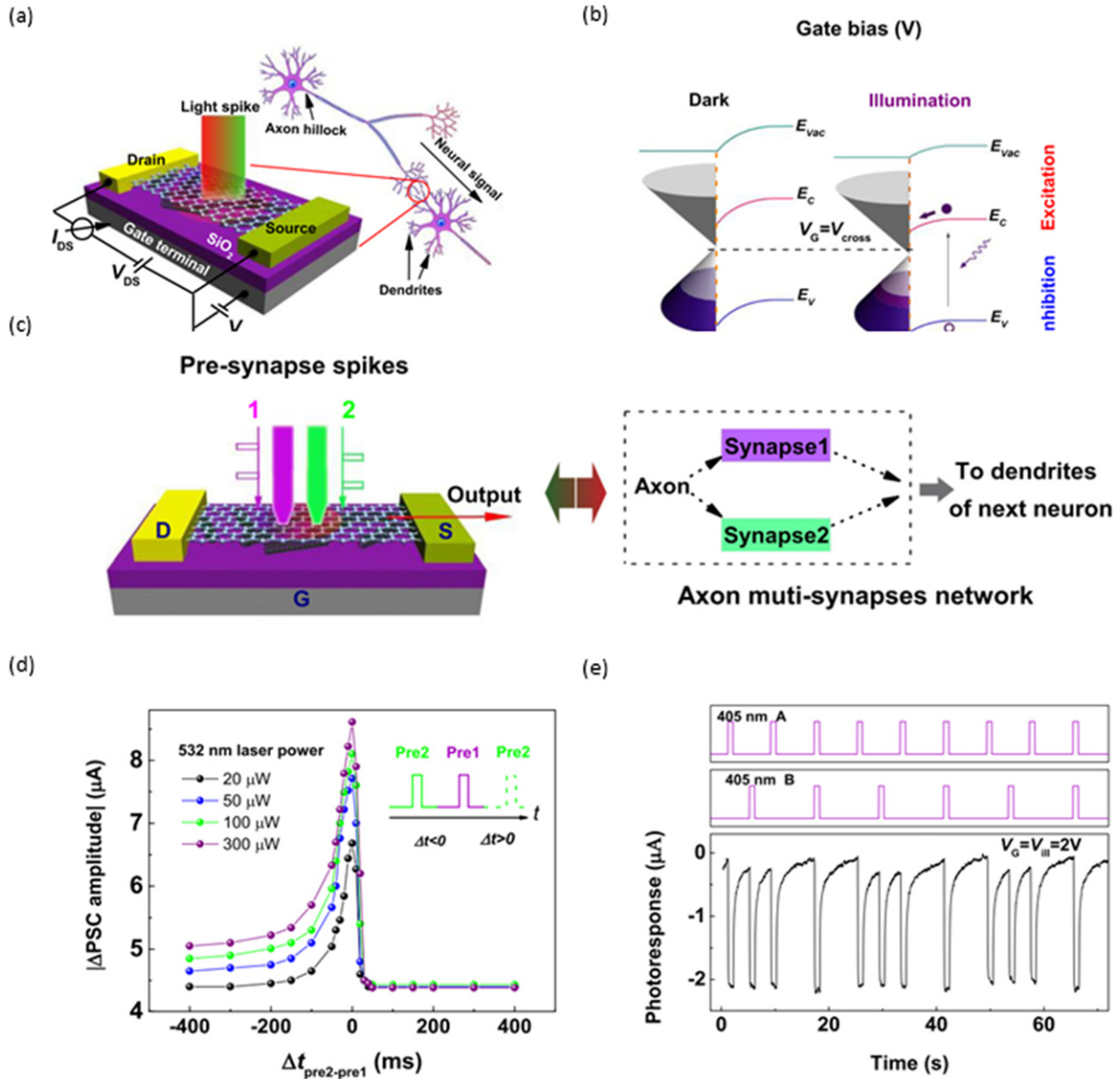


Fig. 11 A Gr-based phototransistor is used for emulating synaptic functions. (a) Schematic illustration of the structure of biological synapses and the process of information transmission in biological synapses. (b) Energy band diagram of interface between Gr and SWNTs. (c) The biological multi-neuron information transmission process and the proposed artificial axon-multi-synapses network. (d) The amplitude of ΔPSC changes with time interval ($\Delta t_{pre2-pre1}$) under different light stimuli. (e) "NOR" logic using two light signals with wavelength of 405 nm. Reproduced from Qin, S., Wang, F., Liu, Y., *et al.*, 2017. A light-stimulated synaptic device based on graphene hybrid phototransistor. *2d Materials* 4, 3.

voltage with negative gate bias. Each synapse contains two transistors using a common source electrode, realizing the modulation of synaptic weight through applying electrical pulses on drain and gate electrodes with different time intervals. This artificial synapse array successfully realized STDP and pattern recognition.

Qin *et al.* (2017) developed a light-stimulated bottom gate synaptic transistor that utilized the strong light absorption of graphene (Gr)/single-walled carbon nanotubes (SWNTs) heterostructure (Fig. 11(a)). Light stimuli can generate several photocarriers in graphene channel, which contribute to the change of channel conductance. The graphene will be p-doping by semiconducting SWNTs in the dark, while under illumination, photogenerated electrons in semiconducting SWNT are transfer to Gr, while the holes are still trapped in the SWNT. The gate bias modulates synaptic excited/depressed time by controlling the density of trap in the Gr/SWNTs interface and substrate (Fig. 11(b)). Furthermore, optical spike processing, such as “NOR” (Fig. 11(c-e)) were demonstrated.

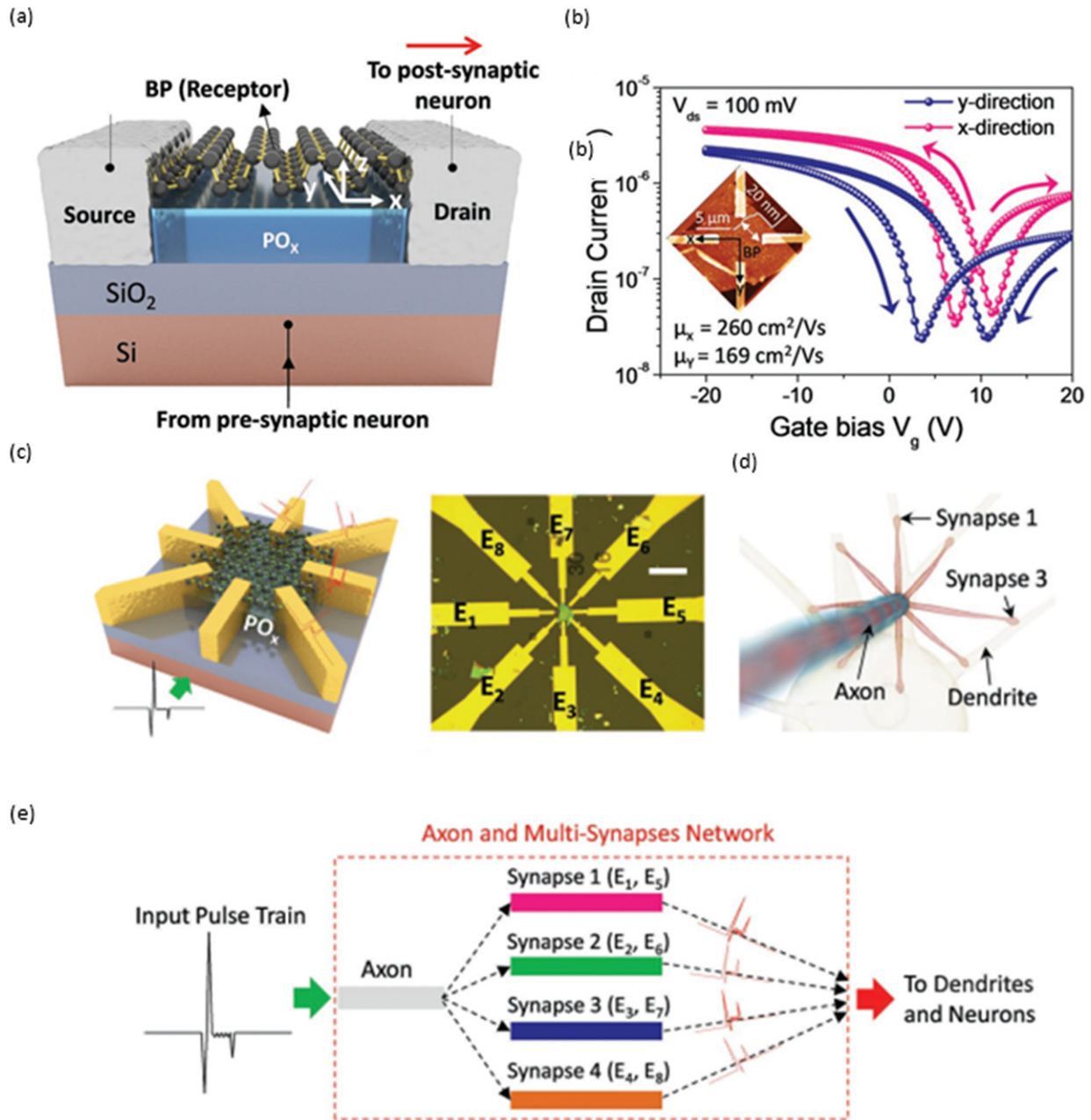


Fig. 12 BP synaptic device. (a) The structure of the proposed device. (b) Transfer curves in different directions of anisotropic BP. (c) Left: The schematic diagram, Right: optical image (right) of BP axon-multi-synapses network. (d) Biological axon-multi-synapses network. (e) The real-time recording of weight changes of synapses. Reproduced from Tian, H., Guo, Q., Xie, Y., *et al.*, 2016. Anisotropic black phosphorus synaptic device for neuromorphic applications *Advance Materials* 28 (25), 4991–4997.

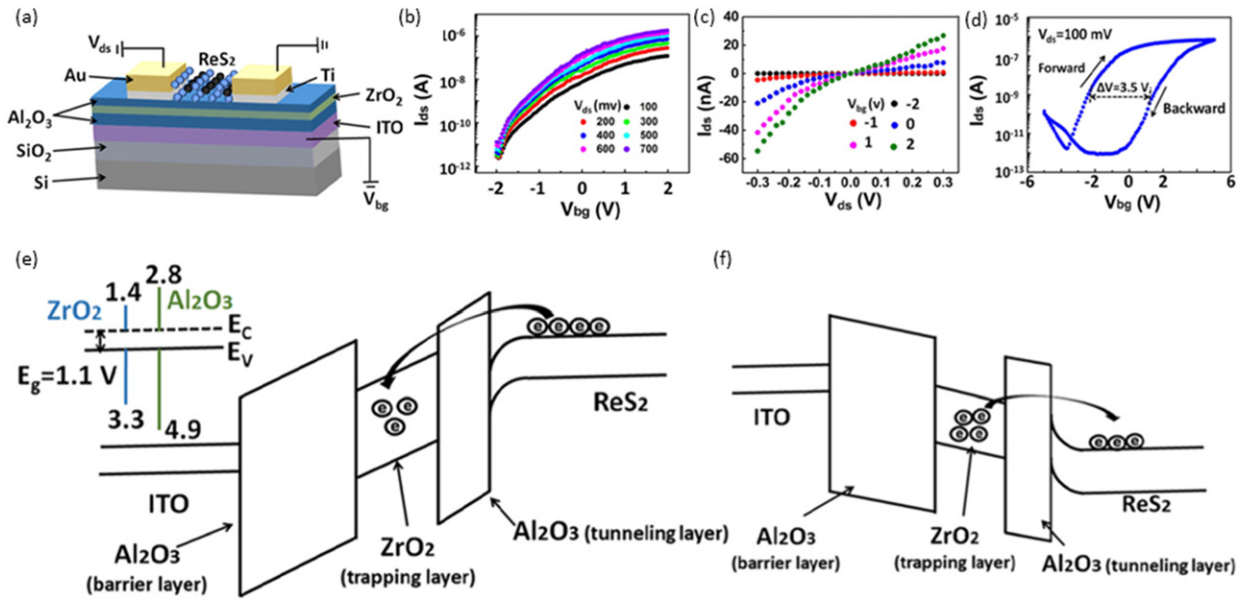


Fig. 13 ReS₂ charge trapping synaptic device. (a) Schematic diagram of ReS₂ device. (b) Transfer curves under a fixed V_{ds} ranging from 200 mV to 700 mV with step of 100 mV. (c) Output curves at fixed V_{bg} ranging from -1 – 2 V with step of 1 V. (d) Hysteresis loop with sweep ranging from -5 – 5 V. The V_{ds} is kept at 100 mV. (e–f) Energy band diagram under the applied back gate voltage with different polarity. (e) under positive gate voltage. (f) under negative gate voltage. Reproduced from Fan, Z.-H., Zhang, M., Gan, L.-R., *et al.*, 2020. ReS₂ charge trapping synaptic device for face recognition application. *Nanoscale Research Letters* 15 (1).

Tian *et al.* proposed an anisotropic black phosphorus (BP) synaptic transistor (Tian *et al.* 2016) (Fig. 12(a, b)). Native phosphorus oxide (PO_x) materials were used as interfacial layer, trapping charges which origin from BP channel under positive bottom gate bias. Consequently, the conductance of p-type BP channel increases with applied voltage. Due to the trapped charge can't be released in the short time after the gate bias end, STM can be gained. Due to the charge transfer of two BP devices, transfer curves in different directions of anisotropic BP exhibit clear hysteresis. Furthermore, an axon-multi-synapses network that took advantage of the anisotropic property of BP was developed (Fig. 12(c, d)). To mimic 4 synapses in one device, 4 pairs of source/drain electrodes were used in different orientations. Hence, the network had four different synaptic weights for transmitting information, which has successfully mimicked the function of axon (Fig. 12(e)).

According to energy band difference between zirconium dioxide (ZrO₂) and Al₂O₃ (Fig. 13(e)), the rhenium disulfide (ReS₂) transistor (Fan *et al.* 2020) where ZrO₂ and Al₂O₃ were respectively used as electron capture layer and tunneling/barrier layer was proposed (Fig. 13(a–c)). The positive gate voltage induces that the electron in channel will flow through Al₂O₃ and be trapped by the defects of ZrO₂ under external electric field, resulting the strong output response (I_{DS}). The trapped electrons that get enough energy will release to the channel through the Al₂O₃ under applied negative back gate bias. Because of the large memory window (Fig. 13(d)), linear EPSC curve and highly stable conductance state, face image recognition was successfully implemented on this synaptic transistor and the accuracy rate up to 100%.

Ion migration

In the electric double layer/electrochemical synaptic transistors, free carriers are orderly moving in the gate electrolyte under the gate voltage, to change channel conductivity. The gate electrode and channel can be treated as presynaptic terminal and postsynaptic terminal, respectively. In the meantime, the channel conductance can be treated as synaptic weight. The electric double layer (EDL) transistor is that the carriers in the electrolyte are accumulating at interface of semiconductor/gate electrolyte by the electrostatic coupling effect under external electrical field. However, for electrochemical synaptic device, the ions can penetrate into the channel through gate electrolyte, finally changing channel conductance, which is called as electrochemical dopant (Jiang *et al.* 2017, Jiang *et al.* 2019, Yang *et al.* 2018, Zhu *et al.* 2018).

Yang *et al.* (2018) reported an all-solid-state synaptic transistor based on the voltage-induced reversible intercalation (Fig. 14(a)). The α -MoO₃ nanosheets which got by mechanical exfoliation were used as channel material. Li-ion electrolyte (lithium perchlorate) was used as gate electrolyte, covering these synaptic terminals (Fig. 14(b)). The Li ions of electrolyte are easy to move under the appropriate gate voltage. In the electrolyte, the Li ions are migrating into the electrolyte/channel interface under positive gate bias (i.e., electrostatic process). As the amplitude of presynaptic signal increases, the Li ions which act as dopant will intercalate into the channel (α -MoO₃), resulting an increase in free electron in the channel, finally increasing channel conductance. Above process is called as electrochemical doping. As the gate voltage reduces (Fig. 14(d)), the Li ions would drift back due to the concentration variation. However, due to thermodynamical stability of the Li_xMoO₃, a large negative voltage is needed for driving all of Li ions back to initial state, resulting the large hysteresis window. As widely acknowledged, the large hysteresis window is

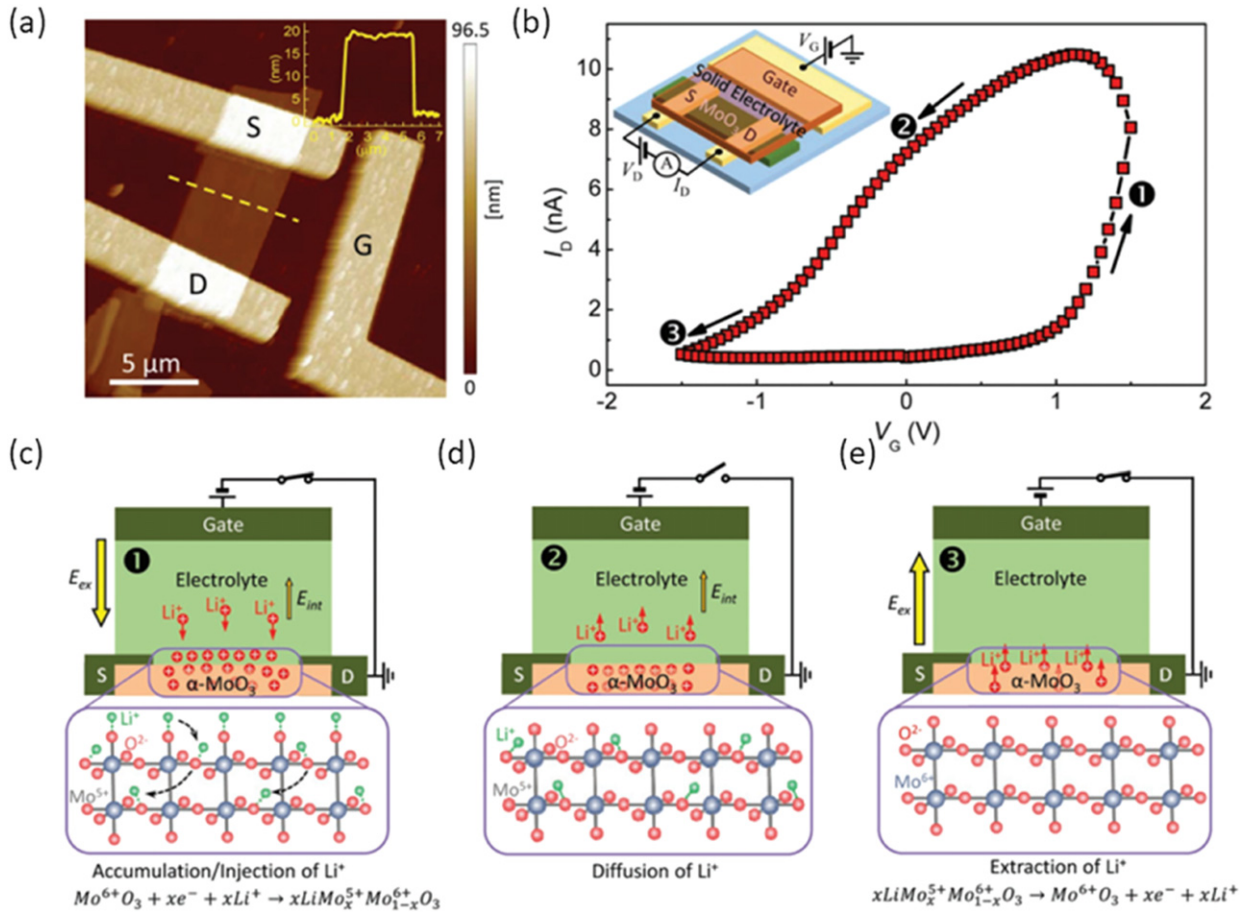


Fig. 14 All-Solid-State Synaptic Transistor. (a) Atomic force microscopy image of the transistor. (b) Hysteresis loop with sweep range from -1.5 – 1.5 V. The inset schematically illustrates the device structure and measurement setting. (c–e) Li ions moving process under the different gate voltage. (c) Under large positive gate bias. (d) The gate bias is removed. (e) Under negative gate bias. Reproduced from Yang, C.-S., Shang, D.-S., Liu, N., *et al.*, 2018. All-solid-state synaptic transistor with ultralow conductance for neuromorphic computing. *Advanced Functional Materials* 28, 42.

helpful to mimic synaptic function and maintain stable conductance state. In the proposed device, Li ions are fully retracted under the negative bias with -1.5 V (Fig. 14(e)), resulting the decrease of the conductance to the initial value. By utilizing experimental measured long-term plasticity characteristics, the simulation about handwritten digit recognition based on the transistor crossbar array was proposed, 94.1% recognition accuracy was achieved.

A multiple-gate MoS_2 EDL synaptic device was proposed by Jiang *et al.* (2017) (Fig. 15(a–d)) and realized some basic synaptic functions (Fig. 15(h)). Furthermore, with multiply driving gates and one modulatory gate, the conversion between the “AND” and “OR” logic (Fig. 15(e–g)) and spike-dependent logic operation, multiplicative neural coding are also experimentally demonstrated. The MoS_2 and poly(vinyl alcohol) (PVA) were used as channel material and gate dielectric, respectively. Compared with traditional dielectrics, PVA electrolyte has more mobile charged ions that are benefit to enhance the electrostatic control ability of gate electrodes and realize low operation voltage. The positive gate voltage facilitates more protons to accumulate at the electrolyte/channel interface, and then mirror the electrons with equal densities in the channel. Such accumulation is reversible process. After the gate bias is removed, the protons at the interface will drift back (Wan *et al.* 2013). Furthermore, the authors have demonstrated that the relationship between operation speed and distance that between channel and the gate electrode in such EDL synaptic device by frequency-dependent phase angle measurement.

Ferroelectric transistors

As an important dielectric, ferroelectric materials with spontaneous polarization ability. As similar to the others materials, the external electric field could influence the polarization strength and direction. In the initial state, the ferroelectric domains have random polarization directions, without polarization strength. The polarization direction gradually becomes ordered with increasing polarization strength through applying external voltage. The polarization strength would get the maximum value when the amplitude of applied voltage is large enough. If the external electric field is removed, there will be the remaining polarization strength since the coupling effect of electric dipole moment. Generally speaking, the ferroelectric property only exists under a certain temperature which is called Curie temperature/Curie point otherwise the material will not have spontaneous polarization.

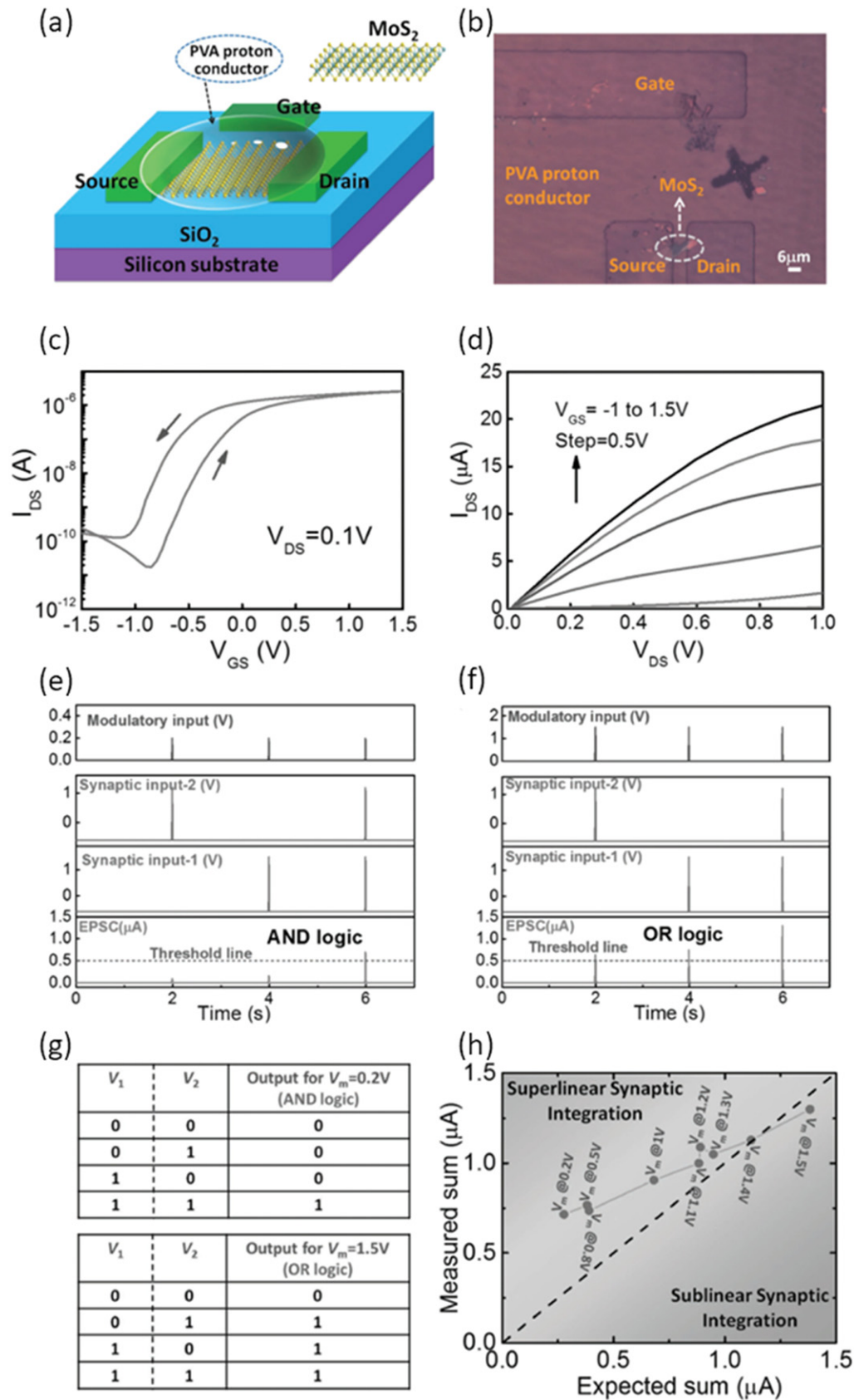


Fig. 15 Multiple-gate MoS₂ EDL synaptic transistor. (a) A schematic diagram of proposed synaptic transistor. (b) An optical image of MoS₂ synaptic transistor. (c) Transfer curves under a fixed V_{DS} with amplitude of 0.1 V. (d) Output curves with fixed V_{GS} ranging from -1–1.5 V with step of 0.5 V. (e) The time response of "AND" logic. (f) The time response of "OR" logic. (g) True tables for "AND" logic (upper) and "OR" logic. (h) The measured sum is described as a function of expected sum. Reproduced from Jiang, J., Guo, J., Wan, X., *et al.*, 2017. 2D MoS₂ neuromorphic devices for brain-like computational systems. *Small* 13, 29.

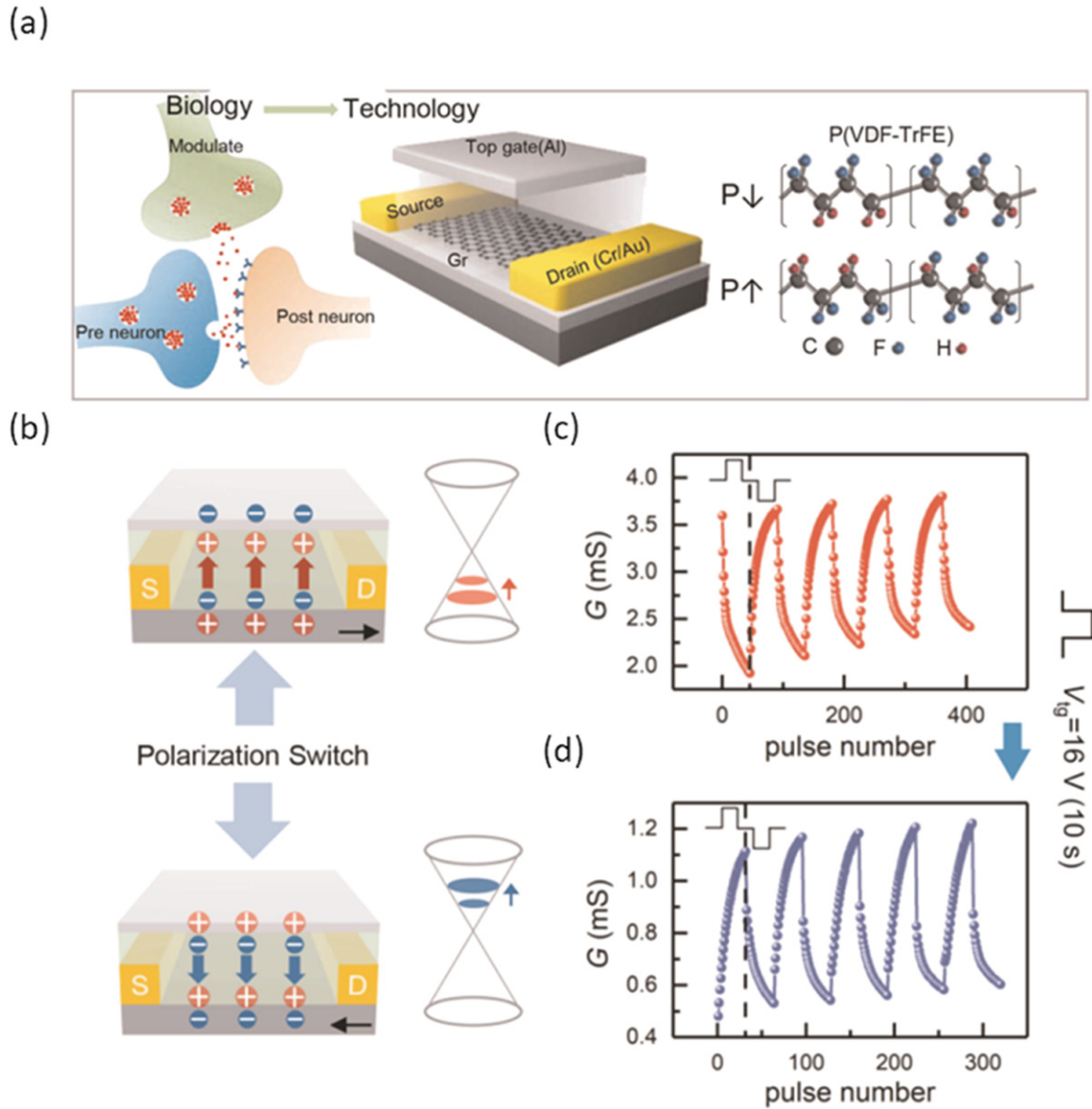


Fig. 16 A graphene-ferroelectric transistor. (a) Schematic view of proposed transistor. (b) Left: schematic illustrates the process of tuning GrFeFET to be potentiation/ depression synapses. Right: the applied positive gate voltage pulses change the channel conductance. (c, d) Six cycles consist of a series of positive gate voltage pulses and a series of negative gate voltage pulses. Reproduced from Chen, Y., Zhou, Y., Zhuge, F., et al., 2019. Graphene-ferroelectric transistors as complementary synapses for supervised learning in spiking neural network. Npj 2d Materials and Applications 3.

Ferroelectric insulator that characteristic in spontaneous polarization and large dielectric constant is key components in the ferroelectric field effect transistor (Nishitani et al. 2013). The non-volatile conductance states of channel help to emulate synaptic functions. Additionally, every single voltage pulse will slightly change the polarization state to realize multilevel intermediate conductance states. The multilevel non-volatile change can be used to record synaptic weight (Chen et al. 2019, Li et al. 2018, Liu et al. 2019, Luo et al. 2020, Tian et al. 2020, Wang et al. 2018).

Chen et al. developed a graphene-ferroelectric transistor (Chen et al. 2019) (GrFeFET) as complementary synapse. The change of synaptic weight depends on the kind of carrier that dominance within the graphene channel (Fig. 16(a)). P(VDF-TrFE) (PVDF) as one of ferroelectric polymers was used as the gate dielectric. Non-volatile shift of Dirac point in the graphene is caused by the polarization of PVDF. When the positive top gate voltage with small amplitude is applied, the Fermi level of p/n conduction graphene channel will move up, at the same time, the density of hole in p-conduction channel will decrease (depression). However, the density of electron near Fermi level in n-conduction channel will increase (potentiation). Hence, the change of synaptic weight depends on the initial band filling state of the graphene that is made by the residual polarization (Fig. 16(b)). Such transistor exactly utilized zero bandgap feature of graphene to realize the conversion between different conduction addition through ferroelectric polarization under the applied gate voltage (Fig. 16(c, d)).

Conclusion

Neuromorphic computing was proposed in the 1980s but rapidly developed in recent years. It mainly focused on the construction of circuits using silicon-based transistors. However, it is very difficult to realize the device integration in future due to the large consumption in energy. As one of the most emerging materials, 2D materials have large specific surface area and sensitive responsibility of external photoelectric signal, making them attractive in the nanoscale devices. It is very promising for the future applications of artificial neural network and intelligent machine based on the 2D materials-based circuit. In the meantime, the unique optoelectronic properties of 2D heterostructure facilitate the broad implications of 2D materials-based synaptic devices. At the same time, it is helpful to learn from biological insect with simple structure and abundant functions for promoting the landing of the neuromorphic device.

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 PBG *see* photonic band gap guiding (PBG)
 PBS *see* polarization beam splitter (PBS)
 PBT puffy thread *see* polybutylene
 terephthalate (PBT) puffy thread
 PC *see* pyramid compression (PC)
 PCAs *see* printed circuit assemblies (PCAs)
 PCE *see* power conversion efficiency (PCE)
 PCF *see* photonic crystal fiber (PCF);
 plasmon controlled fluorescence
 (PCF)

PCFC *see* photonic crystal fiber couplers
 (PCFC)
 PCMs *see* phase change materials (PCMs);
 phase change memory (PCM)
 PD *see* photodetector (PD)
 PDC *see* polarization-diversity circuit (PDC)
 PDDA *see* poly(diallyldimethylammonium
 chloride) (PDDA)
 PDMS *see* polydimethylsiloxane (PDMS)
 PDT *see* photodynamic therapy (PDT)
 PECVD *see* Plasma-Enhanced Chemical
 Vapor Deposition (PECVD)
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 PLCF *see* photonic LC fiber (PLCF)
 PLD *see* pulsed-laser deposition (PLD)
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 PLS *see* perovskite-like structure (PLS)
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